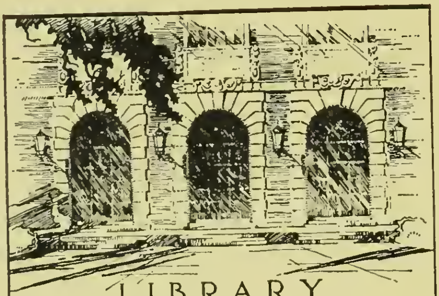

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CHEMISTRY

AMERICAN

CHEMICAL JOURNAL

EDITED BY

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VOL. 8. 1886.

BALTIMORE: THE EDITOR.

ISAAC FRIEDENWALD, PRINTER,
32 S. Paca St.

A2
v8

7200-19

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THE ACTION OF HEAT ON LIQUID PARAFFINS.

BY L. M. NORTON AND C. W. ANDREWS.

The action of heat on the hydrocarbons of the aromatic series has often been studied, but such investigations in the fat series have been confined, with a single exception, to the gaseous hydrocarbons and mixtures of liquid paraffins of unknown composition. Thus, from the work of Thorpe and Young[1] on solid paraffin, of Wagner[2] on refined petroleum, of Liebermann and Burg[3] on petroleum vapors, of Letny[4] on petroleum residuum, of Prunier[5] on gasoline, and of Armstrong[6] and Williams[7] on the products of the Pintsch process for illuminating gas, no information can be gained in regard to the products of the decomposition by heat of any single hydrocarbon. Important investigations of the action of heat on methane, ethane, ethylene and acetylene have been made by Berthelot,[8] and on ethylene by Marchand[9] and Magnus.[10] Berthelot[11] included in his investigations pentane and amylene, and states that when heated in closed retorts to the temperature of the softening of the glass, they gave the lower hydrocarbons of the C_nH_{2n} and C_nH_{2n+2} series, and hydrogen.

---

[1] Ann. d. Chem. **165**, 1.

[2] Dingler, **217**, 64.

[3] Berichte d. deut. chem. Gesell. **11**, 723.

[4] Berichte d. deut. chem. Gesell. **11**, 1210.

[5] Ann. de Chim. et Phys. **5**, 17, 5.

[6] Journ. Soc. Chem. Ind. 1884, 462.

[7] Chem. News, **49**, 197.

[8] Berthelot, La Synthese Chimique.

[9] J. prak. Chem. **26**, 478.

[10] Pogg. Ann. **90**, 1.

[11] Ann. de Chim. et Phys. **4**, 9, 442.

It seemed to us that the action of heat on the liquid paraffins deserved further investigation, and we chose the normal hexane as presenting the most interesting and important study, and have extended our work to isohexane and normal pentane.

The hydrocarbons were prepared from petroleum by fractionation upon an industrial scale.[1] After careful fractionation in the laboratory with the aid of a Hempel's tower 70 cm. high, they were treated with bromine to remove double-bonded hydrocarbons, with fuming nitric acid to remove aromatic hydrocarbons, whenever these were present, dried, and subjected to a final fractionation.

The method of decomposition and purification of the products was essentially the same in each case. The hydrocarbon was decomposed by passing the vapor through a heated glass tube, 15 mm. in diameter, except in the case of isohexane, when a porcelain tube was used. The tube was heated in a combustion furnace 70 cm. long. The hydrocarbon was delivered in a slow stream from a drop-funnel. A pressure of carbonic acid was maintained upon the hydrocarbon to overcome a very annoying back pressure from the decomposition tube. The hydrocarbon was vaporised by the gentle heat in the part of the tube outside the furnace, and the vapors passed on through the tube. The products of the decomposition passed first through a tube one metre long surrounded by ice-water into a receiver also cooled by ice-water, and then through a shorter tube surrounded by a freezing mixture and delivering into the same receiver. By means of these two condensers nearly all of the products boiling above 10° were collected in the receiver. The uncondensed gaseous products from the second condenser were passed into an ammoniacal cuprous chloride solution to absorb all triple-bonded hydrocarbons, then through a dilute solution of acetic acid to retain any ammonia, and finally through a series of flasks containing a solution of bromine in bisulphide of carbon to absorb all double-bonded hydrocarbons. As in no case was any considerable precipitate found in the ammoniacal cuprous chloride solution, the products to be investigated were the liquid in the receiver and the bromides from the absorption flasks.

The former was first carefully fractionated, the portions were then treated separately with bromine, and distilled. The bromides were then distilled under a very low pressure, but the quantities obtained were in all cases so small that no satisfactory purification could be made. The results of the analyses indicate, however, without much doubt, the presence of certain hydrocarbons.

---

[1] We desire to acknowledge our indebtedness to the Jenney Manufacturing Co. of South Boston, refiners, for their kind assistance.

The bromides from the absorption flasks were freed from any excess of bromine, and from the bisulphide of carbon, and then distilled under a very low pressure. The liquid bromides were thus separated from a tarry mass containing a solid bromide which could not be distilled, even under reduced pressure, without decomposition. The distillation was carried to the point at which decomposition began. The liquid bromides were then fractionated, and separate portions were analysed. The solid bromide was extracted from the tar by hot alcohol, crystallised from hot alcohol and sublimed until it showed a constant melting-point.

Normal Hexane.

The normal hexane boiled at 68° and had a specific gravity of 0.6745 at 18° compared with water at 4°. The decomposition was effected at a bright red heat, and was carried on very slowly, in order that it might be as complete as possible. Usually about 25 cc. were decomposed in an hour. Only traces of a precipitate were formed in the ammoniacal cuprous chloride solution, and after a short time the gases were allowed to pass directly from the condenser into the bromine solution.

The weight of the liquid in the receiver was one-tenth of the weight of hexane used. It contained about 12 per cent. of unaltered hexane and small quantities of double-bonded hydrocarbons boiling below 80°. Analysis of the bromides gave 68.17 per cent. bromine, and indicated a mixture of hexylene and amylene bromides. The small fraction boiling above 75°, after treatment with bromine, was proved, by the aniline test, to contain considerable benzol. Nitrobenzol was readily formed at 0°, hence it could not have been derived from hexhydrobenzol.[1] It is certain, therefore, that benzol can be obtained from hexane, though the yield is small. As no acetylene was found among the products of decomposition, it is most probable that the benzol was not formed by the action of heat upon acetylene. Besides hexane, benzol and double-bonded

[1] Weden, Ann. d. Chem. 187, 163.

hydrocarbons, the liquid contained very small quantities of saturated hydrocarbons boiling between 100° and 160°, and some tar.

The bromides from the absorption flasks could not be separated completely by long fractionation under ordinary and reduced pressure. The following analyses were made:

I. 0.1573 gram of portion boiling at 128°–130.5° gave 0.3138 gram of AgBr.

II. 0.3261 gram of portion boiling at 136° gave 0 6314 gram of AgBr.

III. 0.1648 gram of portion boiling at 140°–144° gave 0.3067 gram of AgBr.

	Calculated for $C_2H_4Br_2$.	Found. I.	II.	III.	Calculated for $C_3H_6Br_2$.
Per cent. Br	85.11	84.90	82.39	79.22	79.22

They are, therefore, ethylene and propylene bromides in nearly equal quantities. We were unable to detect the presence of butylene bromide.

The solid bromide crystallised in beautiful colorless needles, insoluble in water, which melted at 112°. Its composition was that of a tetrabrombutane.

I. 0.2154 gram of substance gave 0.0372 gram of H_2O and 0.1028 gram of CO_2.

II. 0.1125 gram of substance gave 0.2255 gram of AgBr.

III. 0.1196 gram of substance gave 0.2403 gram of AgBr.

	Calculated for $C_4H_6Br_4$.	Found. I.	II.	III.
C	12.84	13.01	...	...
H	1.60	1.91	...	...
Br	85.56	...	85.33	85.49

This tetrabrombutane closely resembles in its properties that obtained by Caventon[1] from the products of the decomposition of ordinary amyl alcohol at a red heat, and by Henninger[2] from the butine obtained from erythrite. If identical with this, its constitution is $CH_2Br.CHBr.CHBr.CH_2Br$. Furthermore, it should be identical with that obtained by Prunier[3] from the products of the decomposition of gasoline at a red heat, although Prunier considers his bromide to be derived from the hydrocarbon $CH_3.CH_2.C\vdots CH$, while our compound cannot be derived from a triple-bonded hydrocarbon. It seems probable, also, that it is identical with that obtained by Armstrong[1] from the condensed products of the Pintsch process and with that of Helbing[2] from the liquids of low boiling-point obtained in refining benzol.

---

[1] Comptes Rendus 56, 646.

[2] Bull. Soc. Chim. [2] 19, 145.

[3] Ann. d. Chim. et Phys. 5, 17, 12.

The decomposition of hexane at a red heat gave, therefore, ethylene, propylene, butine, amylene, hexylene, benzol and gases not absorbed by bromine.

We next undertook to find the temperature at which this decomposition begins, and to investigate the products obtained at a comparatively low temperature. The apparatus used was the same as above described, except that the glass decomposition tube was surrounded by an iron pipe 5 cm. in diameter, and slightly longer than the combustion furnace. The temperature of the air in the pipe was determined approximately by means of a calibrated air-thermometer.[3] At 550° no gases were given off, and the hexane was recovered unchanged. At 600° the formation of gases was not observed, but the hexane recovered was found to contain traces of unsaturated compounds, indicating that decomposition had begun. At a little below 700° gases began to pass through the apparatus, and an investigation of the products at this temperature was made. They were collected as in the previous case. There was no precipitation in the ammoniacal cuprous chloride solution.

The liquid in the receiver began to boil at 57°, and was separated into portions boiling at 57°–64°, 64°–70° and 70°–80°. The bromide from the lowest portion contained 72.61 per cent. of bromine, and was probably a mixture of butylene and amylene bromides. Its specific gravity at 0° was 1.77, while that of butylene bromide is 1.8503, and that of amylene bromide 1.7087, at the same temperature.[4] The bromide from the portions boiling at 64°–80° contained 67.07 per cent. of bromine, and was probably a mixture of amylene and hexylene bromides.

The most careful tests failed to detect benzol in any of the fractions, and we are convinced that it is not formed from hexane at the temperature of the experiment. The chief constituent of the liquid was undecomposed hexane.

The bromides from the absorption flasks upon fractionation separated into two portions of tolerably constant boiling-points, one at 140°–145°, the other, much smaller in quantity, at 150°–155°. The analysis resulted as follows:

---

[1] Jour. Soc. Chem. Ind. 1884, 462.

[2] Ann. d. Chem. 172, 291.

[3] Berthelot, Méchanique Chimique I, 301.

[4] Saytzeff, Ann. d. Chem. 179, 332 and 308.

I. 0.2448 gram of substance boiling at 140°–145° gave 0.4562 gram of AgBr.

II. 0.2370 gram of substance boiling at 150°–155° gave 0.4323 gram of AgBr.

	Calculated for $C_3H_6Br_2$.	Found. I.	Found. II.	Calculated for $C_4H_8Br_2$.
Per cent. Br	79.22	79.33	77.62	74.06

The second portion undoubtedly contained butylene bromide, but the quantity was not sufficient to permit its complete separation from the propylene bromide. Ethylene bromide was not observed. The solid bromide melted constantly at 116°, and proved upon analysis to be a tetrabrombutane.

I. 0.1073 gram of substance gave 0.2141 gram of AgBr.

	Calculated for $C_4H_6Br_4$.	Found.
Per cent. Br	85.56	84.92

The bromide was more easily purified than in the previous case, and we attribute the difference in melting-point to the greater purity of the latter product.

The decomposition of hexane at about 700° gave, therefore, propylene, butylene, amylene, hexylene, butine and gases not absorbed by bromine.

Isohexane.

The isohexane $CH_3.CH_2.CH_2.CH:(CH_3)_2$ was obtained by fractionation from gasoline. It boiled at 64°. A red heat was employed for its decomposition, and the only change in apparatus was the substitution of a porcelain tube 10 mm. in diameter for the glass one. A very slight deposit of carbon was formed in the tube. The products were collected as usual. The ammoniacal cuprous chloride solution showed traces of a precipitate.

The liquid in the receiver was fractionated into portions boiling at 40°–60°, 60°–76°, and a small residue above 76°. The bromide from the lowest portion boiled at 86°–90° under a pressure of 52 mm., and contained 73.2 per cent. of bromine. The bromide from the second portion boiled at 99°–102° under 42 mm. pressure, and contained 66.8 per cent. of bromine. The first was probably butylene bromide, and the second hexylene bromide with a little amylene bromide. The remainder of the liquid consisted of undecomposed isohexane and a small quantity of tar.

The bromides from the absorption flasks were separated from the solid bromide by distillation at the ordinary pressure. Portions boiling at 130.5°, 136° and 141.5° were analysed.

I. 0.3100 gram of portion boiling at 130.5° gave 0.6177 gram of AgBr.

II. 0.3333 gram of portion boiling at 141.5° gave 0.6231 gram of AgBr.

	Calculated for $C_2H_4Br_2$.	Found.		Calculated for $C_3H_6Br_2$.
		I.	II.	
Per cent. Br	85.11	84.8	79.5	79.22

The portion boiling at 136° contained 80.5 per cent. of bromine, indicating a mixture in which propylene bromide predominated.

The solid bromide was crystallised repeatedly from alcohol until it melted constantly at 107.5°. It crystallised in pearly scales.

0.2151 gram of substance gave 0.4322 gram of AgBr.

	Found.	Calculated for $C_4H_6Br_4$.
Per cent. Br	85.50	85.56

The low melting-point, which was not raised by sublimation, and the different crystalline form make it improbable that this bromide is identical with the one obtained from normal hexane.

The decomposition of isohexane at a red heat gave, therefore, ethylene, propylene, butylene, amylene, hexylene, butine and gases not absorbed by bromine.

Normal Pentane.

The pentane was obtained from petroleum by fractional distillation. It boiled between 35° and 37.5°; its specific gravity at 17° was 0.6323 compared with water at the same temperature. The apparatus and method of decomposition were the same as for normal hexane. The decomposition was more rapid and complete than in the case of hexane. Carbon was deposited in the decomposition tube. The ammoniacal cuprous chloride solution showed mere traces of a precipitate.

The amount of the liquid in the receiver was very small, about 6 per cent. of the pentane used, and the larger part of it was undecomposed pentane and tar. Unsaturated hydrocarbons were present, but in quantities too small for identification. Benzol was not present.

Portions of the bromides from the absorption flasks boiling at 128°–130° and 140°–144° were analysed.

I. 0.2040 gram of portion boiling at 128°–130° gave 0.4080 gram of AgBr.

II. 0.2281 gram of portion boiling at 140°–144° gave 0.4275 gram of AgBr.

	Calculated for $C_2H_4Br_2$.	Found. I.	Found. II.	Calculated for $C_3H_6Br_2$.
Per cent. Br	85.11	85.13	79.75	79.22

The solid bromide melted constantly at 113°, and was a tetrabrombutane.

I. 0.1079 gram of substance gave 0.2172 gram of AgBr.

II. 0.4118 gram of substance gave 0.1933 gram of CO_2 and 0.0620 gram of H_2O.

	Calculated for $C_4H_6Br_4$.	Found. I.	Found. II.
Br	85.56	85.67	...
C	12.84	...	12.80
H	1.60	...	1.68

We know no reason to doubt the identity of this tetrabrombutane with the one obtained from normal hexane.

The decomposition of normal pentane at a red heat gave, therefore, ethylene, propylene, butine, traces of other unsaturated hydrocarbons, and gases not absorbed by bromine. Berthelot[1] obtained, by the prolonged action of heat on pentane, methane, ethane and hydrocarbons C_nH_{2n+2} from propane to pentane, ethylene and hydrocarbons C_nH_{2n} from propylene to amylene, hydrogen, small amounts of tarry hydrocarbons and traces of acetylene. It is probable that the difference between these results is due to the different conditions of the experiments.

The comparative yield of the various products in these decompositions is shown by the following table:

	Normal Hexane, red heat.	Normal Hexane, 700°.	Isohexane, red heat.	Normal Pentane, red heat.
Hexylene,	very small	very small	very small	
Amylene,	very small	very small	traces	traces ?
Butylene,	none	small	moderate	
Propylene,	large	large	large	large
Ethylene,	large	none	large	large
Butine,	small	small	small	small
Benzol,	small	none	none	none
Gases not absorbed by bromine,	large	moderate	large	large

---

[1] Ann. d. Chim. et Phys. **4**, 9, 442.

The liquid paraffins furnish principally, under the conditions described, hydrocarbons of lower molecular weight. The relative amounts, however, vary with the temperature employed. The tendency to form by condensation hydrocarbons of higher molecular weight is very slight. The frequent occurrence of butines among the products of such decompositions makes a further study of their structure desirable.

In this investigation we have been ably assisted by Messrs. H. P. Talbot and H. W. Tyler, and we desire to acknowledge our great indebtedness to them.

MASS. INSTITUTE OF TECHNOLOGY, BOSTON.

A NEW APPARATUS FOR MEASURING GASES AND MAKING GAS ANALYSES.

BY E. H. KEISER.

In recent years the methods of gas analysis for industrial and technical purposes have been greatly simplified and improved, and are being used more and more extensively in manufacturing establishments. Much less progress has, however, been made in the more accurate scientific methods of gas analysis. While the labors of Orsat, Bunte, Winkler and Hempel have resulted in bringing the methods of industrial gas analysis to such a condition of perfection that the composition of any gas mixture may be determined with great rapidity, and with a degree of accuracy sufficient for all manufacturing purposes, nevertheless, when more accurate results are required, recourse must be had to the older eudiometric methods of Bunsen. Admirable as these methods are, it cannot be denied that great skill is required to carry them out, and to obtain good results, scrupulous attention must be given to all the minute details and precautions. The measurements being made in graduated eudiometers, it is necessary that the eudiometers should be calibrated, and tables of corrected readings constructed, before an analysis is made. There are inconveniences connected with the introduction and removal of absorbing reagents, and as solid reagents are nearly always used, the absorption requires considerable time. In brief, the method is not at all adapted to making a series of rapid and yet accurate analyses.

Numerous forms of apparatus have been devised to overcome the difficulties of the Bunsen method. Among others, Regnault and Reiset,[1] Frankland and Ward,[2] Doyère,[3] and recently Hempel,[4] have constructed instruments by means of which analyses can be made with as great accuracy as by the Bunsen method, and with much greater rapidity. Liquid instead of solid absorbing reagents are used, and the graduated measuring tubes are surrounded by water, so that an equality of temperature between the gas and water is rapidly obtained. All of these gas-measuring instruments are more or less complicated in construction. Graduated glass measuring tubes are used, thus necessitating a previous calibration. Most of them occupy a large space, and must be kept in separate rooms especially devoted to gas analysis.

It seemed therefore desirable to construct a simple gas-measuring apparatus which would be compact in form, which might be easily carried about and used at any place, and yet be capable of measuring gas volumes with great accuracy. Long graduated glass tubes and graduated vessels of all kinds were discarded, and an instrument was constructed upon the principle of determining the volume of a gas from the weight of mercury which it displaces at a known temperature and pressure. From the weight of mercury displaced the volume of the gas can be determined with much greater accuracy than by a direct reading on a graduated glass eudiometer.

The accompanying cut shows the construction of the measuring apparatus and the absorption pipette. *A* is the measuring apparatus, *B* is the absorption pipette; *a* and *b* are glass bulbs of about 150 cc. capacity. They are connected at the bottom by a glass tube of 1 mm. bore, carrying the three-way stop-cock *d*. The construction of the key of the stop-cock is shown in the margin. One hole is drilled straight through the key, and by means of this the vessels *a* and *b* may be made to communicate. Another opening is drilled at right angles to the first, which communicates with an opening extending through the handle, but does not communicate with the first opening. By means of this, mercury contained in either *a* or *b* may be allowed to flow out through the handle *d* into a cup placed beneath. The bulb *b* is contracted at the top to an opening 20 mm. in diameter. This is closed by a rubber stopper carrying a bent glass tube, to which is attached the rubber pump *e*. To a second glass tube passing through the stopper, a short piece of rubber tubing with a pinch-cock is attached. By means of the pump *e* air may be forced into or withdrawn from *b*, as one or the other end of the pump is attached to the glass tube.

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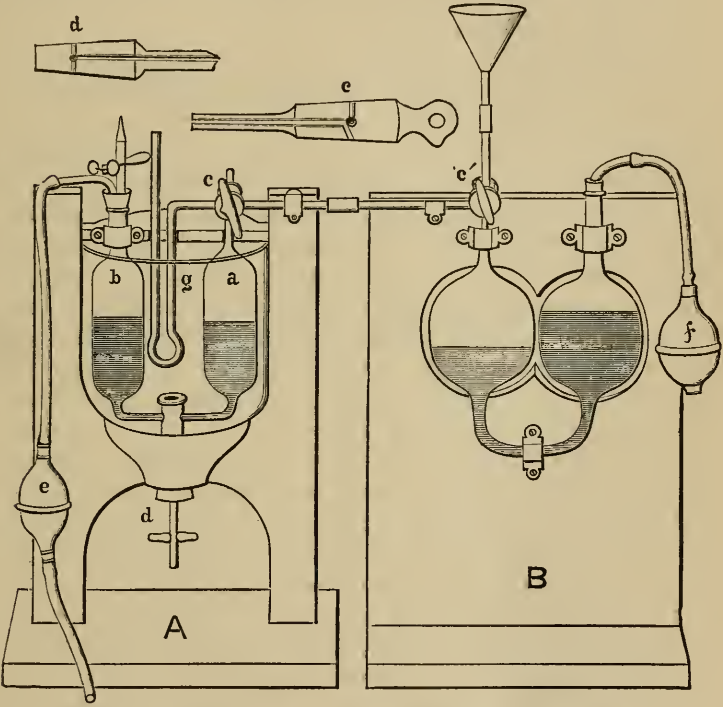
[1] Regnault and Reiset, Ann. Chim. Phys. [3] **26**, 333.

[2] Frankland, Journ. Chem. Soc. 1868, 109.

[3] Doyère, Ann. Chim. Phys. [3] **28**, 1.

[4] Hempel, Analyse der Gase, Braunschweig, 1880.



The bulb *a* terminates at the top in a narrow glass tube, to which is fused the three-way stop-cock *c*. The construction of the key of this stop-cock is also shown in the cut. By means of it the vessel *a* may be allowed to communicate with the outside air, or with the tube passing to the absorption pipette, or with the gauge *g*. The gauge *g* is a glass tube having a bore 1 mm. in diameter and bent, as shown in the figure. By pouring a few drops of water into the open end of this tube a column of water several centimeters high in both limbs of the tube is obtained. This serves as a manometer, and enables the operator to know when the pressure of the gas equals the atmospheric pressure. To secure a uniform temperature, the bulbs *a* and *b* are surrounded by water contained in a glass vessel. This vessel for holding water is merely an inverted bottle of clear glass from which the bottom has been removed. The handle of the stop-cock *d* passes through a rubber stopper in the neck of the bottle. A thermometer graduated to $\frac{1}{5}$° is placed in the water near the bulb *a*. The whole apparatus is supported upon a vertical wooden stand.

The absorption pipette *B* consists of two nearly spherical glass bulbs of about 300 cc. capacity. They communicate at the bottom by means of a glass tube, 3 mm. inside diameter. *c′* is a two-way stop-cock. The holes in the key are drilled at right angles, so that the tube which connects with the measuring apparatus may be put in communication either with the funnel or with the absorption bulb. The funnel is of service in removing air from the tube which connects the measuring apparatus with the absorption pipette. By pouring mercury or water into the funnel and turning the stop-cocks *c′* and *c* in the proper directions all the air is readily removed. *f* is a rubber pump used in transferring gas from *B* to *A*. The lower part of the pipette contains mercury, which protects the reagent from the action of the air.

To measure the volume of a gas the vessel *a* is filled completely with pure mercury. This is easily accomplished by pouring the mercury into *b*, and then, after turning *c* until *a* communicates with the outside air, forcing it into *a* by means of the pump *e*. Any excess of mercury in *b* is then allowed to flow out through the stop-cock *d*. When *a* and *b* are now placed in communication the mercury will flow from *a* to *b*, and gas will be drawn in through the stop-cock *c*. The volume of mercury which flows into *b* is equal to the volume of gas drawn into *a*. When the mercury no longer rises in *b*, and it is desired to draw in still more gas into *a*, then it is only necessary to exhaust the air in *b* by means of the pump *e*. After the desired quantity of gas has been drawn into *a* the stop-cock *c* is closed. After standing a few minutes the temperature of the gas becomes the same as that of the water surrounding *a*. The pressure of the gas is then made approximately equal to atmospheric pressure by allowing the mercury to flow out of *b* into a weighed beaker placed beneath the stop-cock *d* until it stands at nearly the same level in both *a* and *b*. Communication is now established between *a* and *g*, and by means of the pump *e* the pressure can be adjusted with the utmost delicacy until it is exactly equal to atmospheric pressure. The stop-cock *d* is then closed, and the remainder of the mercury in *b* is allowed to flow out into the beaker. The weight of the mercury displaced by the gas divided by the specific gravity of mercury at the observed temperature gives the volume of the gas in cubic centimeters.

If it is desired to remove any constituent of the gas by absorption, a pipette *B*, containing the appropriate reagent, is attached to the measuring apparatus. All the air in the connecting tube is expelled by pouring mercury into the funnel and turning the stop-cocks *c′* and *c* so that the mercury flows out through *c*. A little more than enough mercury to expel the gas in the vessel *a* is poured into *b*. The small quantity of air which is confined in the tube connecting *b* with the stop-cock is removed by allowing a few drops of mercury to run out through *b*. Then *a* and *b* are placed in communication. The stop-cocks *c* and *c′* are turned so that the gas may pass into the pipette, the mercury which filled the connecting tube passes into the absorbing reagent and unites with that which is already at the bottom of the pipette. The transfer is facilitated by the pump *e*. After absorption the residual volume is measured in the same way that the original volume was measured. *a* is completely filled with mercury from the upper to the lower stop-cock, and all the mercury in *b* is allowed to run out; the gas is then drawn back into the measuring apparatus, the last portion remaining in the connecting tube being displaced by means of mercury from the funnel. The volume is then determined as before.

The calculation of the results of an analysis is very simple. If the temperature and pressure remain the same during an analysis, as is frequently the case, then the weights of mercury obtained are in direct proportion to the gas volumes, and the percentage composition is at once obtained by a simple proportion.

If the temperature and pressure are different when the measurements are made, it is necessary to reduce the volumes to 0° and 760 mm. The following formula is then used:

$$V' = \frac{W(H-h)}{D(1 + .00367 \times t)760},$$

in which

W = weight of mercury obtained (in grams),
D = specific gravity of mercury at t°,
t = temperature at which the gas is measured,
H = height of the barometer,
h = tension of aqueous vapor,
V' = reduced gas volume (in cubic centimeters).

In all the measurements made with the apparatus the gas is saturated with aqueous vapor, because it comes in contact with the water in the manometer *g*.

The following experiments were made to test the accuracy of the instrument. A quantity of air was drawn into the measuring bulb and its volume determined. The air was then transferred to an absorption pipette which contained only mercury and no reagent. It was then brought back again into the measuring apparatus and its volume redetermined. The following results were obtained:

I.

	Volume at 0° — 760 mm.
Volume of air taken,	57.558 cc.
" after first transfer,	57.567
" " second transfer,	57.570

II.

	At 0° — 760 mm.
Volume taken,	93.216 cc.
" after transferring,	93.229

III.

	At 0° — 760 mm.
Volume taken,	133.473 cc.
" after transferring,	133.490

IV.

	At 0° — 760 mm.
Volume taken,	92.275 cc.
" after transferring,	92.260

V.

	At 0° — 760 mm.
Volume taken,	109.025 cc.
" after transferring,	109.020

VI.

	At 0° — 760 mm.
Volume taken, ...	103.970 cc.
" after first transfer, ...	103.955
" " second transfer, ...	103.980

The apparatus was also tested by making analyses of atmospheric air. It has been shown that the composition of the air varies from day to day.[1] This variation is sometimes as much as .5 per cent. The causes which produce these fluctuations in the composition of the atmosphere are at present but imperfectly understood. It is therefore desirable to have some simple instrument by means of which the composition of the air may be determined rapidly and yet with great accuracy.

The following analyses show that the apparatus here described is well adapted to this purpose. The reagent used to absorb the oxygen and carbon dioxide was an alkaline solution of pyrogallol, prepared by mixing one volume of a 25 per cent. solution of pyrogallol with six volumes of a 60 per cent. solution of potassium hydroxide.

Analysis of Air taken from the Laboratory.

I.

	W	H	t	V′	Per cent. $O + CO_2$.
Air taken,	1738.53	743.37	15.8	116.435 cc.	...
Vol. of nitrogen,	1377.62	743.37	15.8	92.264	20.760
" "	1376.40	743.55	15.75	92.255	20.771

Per cent. of oxygen and carbon dioxide, 20.765.

II.

	W	H	t	V′	Per cent. $O + CO_2$.
Vol. of air,	1708.01	748.08	15.0	115.546 cc.	...
" nitrogen,	1356.04	747.33	15.2	91.564	20.755

Per cent. of oxygen and carbon dioxide found, 20.755.

The following analyses were made with a sample of atmospheric air collected on a subsequent day :

I.

	W	H	t	V′	Per cent. $O + CO_2$.
Vol. of air,	1704.81	754.92	12.2	117.814 cc.	...
" nitrogen,	1348.33	754.78	12.08	93.216	20.877
" "	1344.71	755.92	11.7	93.229	20.868

Per cent. of oxygen and carbon dioxide, 20.872.

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[1] Winkler, Industrie Gase 2, 405. Hempel, Berichte der deutsch. chem. Gesell. **18**, 267.

II.

	W	H	t	V′	Per cent. $O+CO_2$.
Vol. of air,	1669.39	756.30	10.15	116.584 cc.	...
“ nitrogen,	1323.24	755.49	10.05	92.260	20.863
“ “	1322.38	755.30	10.00	92.252	20.870

Per cent. of oxygen and carbon dioxide, 20.866.

The apparatus described in the preceding pages was made for the author, in most excellent manner, by Mr. Emil Greiner, 79 Nassau street, New York.

BRYN MAWR, PA., *December*, 1885.

THE TITRATION OF ACID TUNGSTATES.

BY HERMAN SCHMIDT.

In No. 13 of the "Berichte der deutschen chemischen Gesellschaft," G. v. Knorre publishes some observations on the titration of acid tungstates, or as he calls them, paratungstates. As I have been engaged in the same line of research, I feel prompted to publish the results thus far obtained, in order to indicate my right to labor in this field.

When the salt $12WO_3 5Na_2O+28Aq$ is dissolved in boiling water, the resulting solution has an acid character towards certain indicators. When phenolphthalein and rosolic acid are used, the solution reveals its acid nature; with cochineal solution and orange No. 3, however, the solution is alkaline. The investigation was undertaken in the hope that an acid tungstate might serve as an agent for standardising an alkaline solution. The preliminary results justified this belief, but an extended investigation revealed its fallacy.

2.0840 grams of the pure salt, in which the ratio is 12 of WO_3 to 5 of Na_2O, were dissolved and the solution was diluted to 500 cc., and portions of 50 cc. each were used for experiment. With an ammonia solution and phenolphthalein the change of color is very indistinct. A caustic soda solution containing .6471 gram Na_2O to 100 cc., and a chlorhydric acid solution containing .3478 gram HCl to 100 cc. were used.

Using phenolphthalein as the indicator, 50 cc., containing .2084 gram salt, required 1.25 cc. of the NaOH solution to give a distinct change. The purplish pink color remained unchanged for a minute or two, and then vanished. Successive additions of .02 cc. of alkali restored the color, which vanished again after each addition. This showed conclusively that the titration must be conducted in some other manner.

To determine, however, whether the first change of color was constant for successive titrations, and whether a saturating power corresponding to a definite salt—viz. $12WO_3(5+x)Na_2O$, in which x is an integer between 1 and 7, was indicated, the following experiments with this same solution were made:

Volume of the Solution.	$12WO_3\,5Na_2O+28Aq$ contained.	Soda Solution required.
50 cc.	.2084 gram.	1.25 cc.
"	"	1.26
"	"	1.25

Mean = 1.253 cc. soda solution = 3.88 per cent. Na_2O.

Since the crystallised salt contained 13.62 per cent. H_2O, to calculate the per cent. of Na_2O for the anhydrous salt, the per cent. found must be multiplied by the factor $\frac{100.00}{86.38}$. Result, 4.49 per cent. Na_2O. The ratio which approaches most nearly to this result is $2Na_2O$ for each molecule of $12WO_3\,5Na_2O$, which ratio expressed in percentage is 4.01 per cent. These experiments were performed with cold solutions. When the solution to be titrated was boiled and alkali added until the color appeared, no closely concordant results could be obtained.

If an excess of alkali was added and the solution then boiled, and the excess of alkali neutralised with chlorhydric acid, and alkali again added until the color was just restored, concordant results were obtained. In each case the amount of alkali required to color the same volume of pure water with the same amount of indicator is subtracted from the burette reading.

Experiment.

Volume of the Solution.	Salt contained.	Soda Solution required.
50 cc.	.45863 gram.	8.58 cc.
"	"	8.62
"	"	8.62

Mean = 8.61 cc. = 14.06 per cent. Na_2O.

Calculated on the weight of anhydrous tungstate employed.

Titration with the Use of Aurine as the Indicator.

Volume of the Solution.	Salt contained.	Soda Solution required.
50 cc.	.45863 gram.	8.56 cc.
"	"	8.62
"	"	8.60

Mean = 8.593 cc. = 14.03 per cent. Na_2O.

The molecular weight of $12WO_3 5Na_2O$ is 3094. If then $Na_2O.WO_3$ is a neutral salt, seven molecules of $Na_2O = 434$ are necessary to saturate this acid salt; hence it requires for saturation $\frac{434}{3094} = 14.03$ per cent. Found, 14.06 per cent. and 14.03 per cent. Na_2O.

Upon investigating the subject further it was found that the time during which the solution of the tungstate was boiled with the excess of alkali materially influenced the results of the titration. The following titrations were made with a soda solution containing .2904 gram Na_2O in 100 cc., and a sulphuric acid solution of which 100 cc. corresponded to .2829 gram Na_2O.

8.2832 grams of the crystallised salt $12WO_3 5Na_2O + 28Aq =$ 7.1385 grams of the anhydrous salt were dissolved and the solution diluted to 1000 cc. Portions of 50 cc. each were used for experiment.

Experiments.

No.	Volume of the Solution.	Salt contained.	Alkali required.
1	50 cc.	.41416 gram.	17.27 cc.
2	"	"	17.17
3	"	"	17.25
4	"	"	17.26
5	"	"	17.11
6	"	"	17.04
7	"	"	17.27
8	"	"	17.24
9	"	"	17.26

Mean = 17.21 cc. = .4998 gram Na_2O = 14.00 per cent.

Titrations Nos. 5 and 6 are somewhat low compared with the others. In each experiment the solution was boiled about fifteen minutes with the excess of alkali before neutralising with acid.

Experiments.

6.5325 grams of the crystallised salt = 5.6271 grams of the anhydrous salt were dissolved and the solution diluted to 1000 cc.

No.	Volume of the Solution.	Salt contained.	Alkali required.
1	50 cc.	.32663 gram.	13.52 cc.
2	"	"	13.55
3	"	"	13.49
4	"	"	13.16
5	"	"	13 50
6	"	"	13.53
7	"	"	13.13

Mean of the titrations = 13.41 cc. = .3894 gram Na_2O = 13.86 per cent.

If we reject Nos. 4 and 7, which are low, the mean is 13.52 cc. = .3928 gram Na_2O = 13.97 per cent.

This is hardly justifiable, since all titrations were made in the same way and boiled approximately for the same length of time—viz.: fifteen minutes.

In the following series the time of boiling was slightly varied, as will appear from the fifth column.

7.5467 grams of the crystallised salt = 6.5015 grams of the anhydrous salt were used.

All the titrations were performed as in the foregoing experiments, only in Nos. 1 to 8 inclusive a chlorhydric acid solution was used to neutralise the excess of alkali, and in titrations 9 to 18 oxalic acid was used.

Experiments.

No.	Volume of the Solution.	Salt contained.	Alkali required.	Time of boiling.
1	50 cc.	.37733 gram.	15.96 cc.	12 minutes.
2	"	"	15.97	15
3	"	"	15.68	15
4	"	"	15.88	15
5	"	"	15.90	15
6	"	"	15.86	15
7	"	"	15.86	15
8	"	"	15.99	15
9	"	"	15.70	15
10	"	"	15.87	15
11	"	"	15.81	17
12	"	"	15.91	15
13	"	"	15.93	15
14	"	"	15.95	17
15	"	"	16.04	15
16	"	"	15.88	15
17	"	"	15.90	15
18	"	"	15.92	15

Mean of titrations = 15.89 cc. = .4614 gram Na_2O = 14.19 per cent.

This percentage is .16 in excess of the theoretical amount. This is easily explained; for if the tungstate solution mixed with the excess of soda is boiled less than twelve minutes, the percentage indicated will be very much too low; if the solution is boiled longer than seventeen minutes the result will be too high.

Thus, after titration No. 1 of the foregoing series was completed, alkali was again added to the solution, and after boiling, the excess was neutralised. 16.30 cc. were then indicated = 14.56 per cent. Na_2O. Alkali was again added, and after boiling the excess was neutralised. 16.38 cc. were then indicated = 14.63 per cent. Na_2O. After titration No. 9 of the foregoing series was completed an excess of alkali was added, and the solution boiled thirty minutes; after neutralising, 17.10 cc. in all of the soda solution were required = 15.27 per cent. Na_2O, when theory required 14.03 per cent. The following titrations will also show that the tungstate may be supersaturated with alkali, and the excess not be indicated by the phenolphthalein solution.

a) To 50 cc. of a solution containing .23196 gram $12WO_3 5Na_2 + 28Aq$ an excess of soda was added, and the solution allowed to stand at the temperature of the room. After four days the excess of alkali was neutralised, and .03398 gram Na_2O = 14.65 per cent. had been saturated. To the same solution an excess of alkali was again added, and after three days the excess was again neutralised. The total amount of alkali indicated was 15.01 per cent.

b) To 50 cc. containing .23196 gram $12WO_3 5Na_2O + 28Aq$ an excess of soda was added. After three days .03595 gram Na_2O = 15.50 per cent. had been saturated. Adding alkali again, and neutralising after six days, .03923 gram Na_2O = 16.91 per cent. were consumed.

It would be interesting to see whether the salt $Na_2WO_4 2H_2O$ would result by evaporating and crystallising the solutions.

After 24 hours, at the ordinary temperature, the normal saturation is usually complete, when the alkali is added to the cold tungstate solution. Thus: 50 cc. containing .56271 gram $12WO_3 5Na_2O + 28Aq$ were mixed with an excess of alkali, and after 24 hours the excess was neutralised. .03944 gram = 14.02 per cent. Na_2O were required for saturation.

In another experiment .03969 gram = 14.11 per cent. Na_2O were required for saturation.

The evidence is complete that the salt above titrated in its anhydrous state has the formula $12WO_3\ 5Na_2O$, and is a member of the metatungstate series to which Dr. Gibbs[1] has added a new member, $16WO_3.3Na_2O.4(NH_4)_2O + 8Aq$, the highest yet discovered. It may still be interesting, however, to observe that all the above titrations agree better with the 12:5 than with the 7/3 ratio. If $7WO_3\ 3Na_2O$ were the formula of the anhydrous salt, then four molecules of Na_2O would be required for saturation. These four molecules, expressed in percentage of the anhydrous salt, are 13.70 per cent. Na_2O. The mean of all the titrations, 14.03, 14.06, 14.00, 13.86, 14.19 per cent. is 14.03 per cent., which is the percentage required by the 12:5 salt.

To a boiling solution of the normal tungstate $Na_2WO_4 + 2Aq$ ordinary acetic acid was added in excess. By the addition of alcohol an oil was precipitated, which readily changed into a crystalline mass. After two crystallisations the product was titrated.

Under these circumstances[2] one of two salts is produced. One has the constitution $10WO_3\ 4Na_2O + 23H_2O$, and the other agrees best with the formula $22WO_3\ 9Na_2O + 51Aq$. Just which was produced in the case I had not the means to decide, as I lacked facilities for quantitative work. The salt on ignition lost 13.79 per cent. H_2O. The salt $10WO_3\ 4Na_2O + 23H_2O$ requires 13.88 per cent. H_2O; and the formula $22WO_3\ 9Na_2O + 51Aq$ requires 13.95 per cent.

Of this salt 5.0009 grams were dissolved, and the solution was diluted to 1000 cc., and 50 cc. were used for each experiment. The titrations were performed exactly as in the foregoing series with the 12:5 salt. Oxalic acid was the standard acid solution employed.

Experiments.

	Time of Boiling with excess of Alkali.	Volume.	Salt present.	Alkali required.
1	15 minutes.	50 cc.	.25005 gram.	10.48 cc.
2	15	"	"	10.48
3	20	"	"	10.52
4	20	"	"	10.73
5	18	"	"	10.50
6	15	"	"	10.43
7	20	"	"	10.48
8	18	"	"	10.38
9	20	"	"	10.45
10	20	"	"	10.53
11	15	"	"	10.18

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[1] Proceedings of the Am. Academy, 1885.

[2] Gibbs, *Ibid.* 1879, pp. 5, 9.

Titration No. 4 is somewhat high, and No. 11 low. No regularity is discernible in the increase of alkali as the time of boiling is increased. As the titrations were made in the same way, equal weights attach to each of them, and it would not be justifiable to reject either No. 4 or 11.

Mean of the eleven titrations = 10.47 cc., corresponding to .06150 gram Na_2O = 14.26 per cent., which were required to saturate the anhydrous salt.

The formula $10WO_3\,4Na_2O$ requires 6 molecules of Na_2O for saturation. This amount expressed in percentage = 14.49 per cent. Na_2O.

The anhydrous salt $22WO_3\,9Na_2O$ requires 13 molecules Na_2O for saturation, or 14.24 per cent. Na_2O.

The percentage of sodic oxide found, 14.26 per cent., agrees best with 14.24 per cent., the amount required by the 22/9 ratio.

It may be observed that neither haematoxylin nor purpurin can be used in these titrations.

Attempts were made to use a solution containing a known weight of pure 12 : 5 tungstate of soda instead of the standard acid solution. No results whatever could be obtained by titrating either in hot or cold solutions. This might have been foreseen, for no closely concordant results could be obtained by saturating a hot acid tungstate solution with an alkali—*i. e.*, adding the alkali until the indicator showed the excess.

Qualitative experiments seem to show that boiling solutions of acid vanadates can be titrated, using either aurine or phenolphthalein as the indicator, and performing the titration as in the case of the acid tungstates.

An excellent end reaction, but no concordant results are obtained when an alkali is added to a cold solution of the 14 : 6 molybdate of ammonium, using aurine as the indicator. Phenolphthalein, on account of the ammonia liberated, would not apply. If the molybdate solution had been boiled with the excess of soda, so that all the ammonia had been driven off, and then the excess of alkali neutralised, perhaps satisfactory results would have been obtained.

I am greatly indebted to Dr. Wolcott Gibbs for the selection of the subject and the many kind suggestions in connection with this work.

CLEVELAND, IA., *Nov.* 26, 1885.

Contributions from the Chemical Laboratory of Harvard College.

XLVII.—A THERMOCHEMICAL ANALYSIS OF THE REACTION BETWEEN ALUM AND POTASSIUM HYDRATE.

BY A. V. E. YOUNG.

PART I.

In the course of a thermochemical study of potassic aluminate, I desired to use as one element of calculation the amount of heat evolved in the following reaction,

$$Al_2(SO_4)_3.K_2SO_4 + 6KOH = 4K_2SO_4 + Al_2(OH)_6,$$

assuming, in accordance with Thomsen's statement, that the alum is equivalent, for this purpose at least, to aluminic sulphate. This quantity is given by Thomsen[1] as 30.528 Calories. He determines it directly by precipitation with potassic hydrate in the calorimeter, and, as a control, determines the heat of precipitation with three molecules of baric hydrate. The results of the two methods agree fairly well. This value is made by the same author the basis for the indirect determination of the formation heat of the chloride and several other compounds of aluminum, and this notwithstanding the fact that he notes the complete precipitation of the aluminic oxide by five molecules of potassic hydrate instead of six, which would appear to indicate the formation of a basic precipitate. He evidently assumes that the addition of six molecules of the hydrate leaves the precipitate free of sulphuric acid, and that the agreement with the result obtained when baric hydrate is used affords confirmation of the assumption. Indeed, in other instances—*e. g.*, sulphates of copper, cobalt and cadmium—when the two methods do not give concordant results, he adopts the result by baric hydrate, and rejects that by potassic hydrate as being untrustworthy by reason of the formation of a basic precipitate. It would seem unsafe to assume, without experimental verification, that baric hydrate may not produce a basic precipitate as well as potassic hydrate, and thus render both methods open to the same objection.

However this may be, the results which I obtained soon led to the suspicion that the reaction with potassic hydrate was not so simple as is indicated by the above equation. One question after another arising which I was unable to answer, I have been led step by step to what may be called a thermochemical analysis of the reaction in question. The first part of the results obtained constitutes the substance of the following paper. At a later date I hope to publish a determination of the precipitation heat of aluminic hydrate by a method free from these objections. The first series of experiments involves the determination of the reaction heat of alum and potassic hydrate, the proportion of the latter present varying from .5 to 10 molecules. This is followed by a parallel series determining the composition of the precipitates obtained in the calorimetric experiments. Before considering in detail the results of the first series, I give a brief description of the calorimetric methods and of the calculations that were used.

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[1] See Thermochemische Untersuchungen **1**, 366.

METHODS AND CALCULATIONS.

The general method of heat measurement is that described by Berthelot. The calorimeter used was made after the specifications given by him,[1] without essential variation. The inner platinum calorimeter has a capacity of somewhat more than 1200 cc. The stirrer is a simple one, a piece of platinum foil fused to a glass rod. The thermometers were made by Baudin, of Paris, especially for thermochemical work, after specifications by Berthelot,[2] and were calibrated by Pernet at the Bureau International des Poids et Mesures. The zero points have been recently redetermined. The three pairs of duplicates taken together give a range of temperature from 0° to 33° C. They are graduated to fiftieths of a degree, and the readings were made, usually with the aid of a small hand lens, to $\frac{1}{200}$ of a degree, and often to $\frac{1}{400}$. The experiments were performed in a large basement room without artificial heat, where, during a portion of the year at least, the temperature conditions were fairly satisfactory. The operation consisted, with but one or two exceptions, in mixing in the calorimeter two portions of liquid of 500 cc. For this measurement two flasks were used, their graduation being verified by weight.

Solutions containing the requisite quantity of constituents were prepared, diluted to somewhat less than 500 cc., and allowed to stand in closed flasks beside the calorimeter until the following day, or perhaps during a longer interval. When ready for the calorimetric determination, one of the prepared solutions was transferred with rinsing to the measuring-flask (care being taken not to change unduly its temperature in the handling) and filled to 500 cc. with distilled water that had stood a day or longer on the same table. It was then poured into the calorimeter and its temperature taken, after thorough stirring, at intervals of five minutes. The change of temperature during this interval should not be more than .02°. At the same time, the second solution having been transferred to the second measuring-flask, its temperature in the flask was taken by a second thermometer in similar manner. Its change likewise should not be more than .02° per interval of five minutes; and it is also important that it should be close to that of the room, which was read from an ordinary thermometer.

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[1] Essai de Mécanique Chimique **1**, 140.

[2] *Ibid.* p. 164.

When the temperature conditions were satisfactory, and the readings duly recorded, the contents of the second flask were poured as quickly as possible into the calorimeter, the mixture thoroughly stirred, and the resultant temperature recorded. The interval between the last reading of the initial temperatures and the first of the resultant temperature was in this series of experiments one and a half or two minutes, and with few exceptions the maximum temperature was reached in this time. Readings were then taken, always with stirring, every minute for about five minutes, and then at an interval of five minutes, in order to have a record of the rate of cooling.

There seems to be one unsatisfactory point in this method of manipulation—namely, the difficulty of obtaining the true temperature of the second volume of liquid while it still remains in the flask, and of transferring it to the calorimeter without consequent change. Experience will convince one of this difficulty in experiments where a variation of .01° is of considerable importance. My habit is to close the flask and shake it as thoroughly as possible before inserting the thermometer, and to see that its temperature at the time shall be such that it need not be left more than five or ten minutes before transferring to the calorimeter. Meantime the flask stands in a loose bag of flannel, supported by a frame that serves as handle, so that the hand itself is distant several inches from the flask. Nevertheless, I have not infrequently obtained apparently accidental results which varied from the mean notably more than the average variation, and of which the difficulty just described seems the probable cause. I hope later on to reduce, if not to eliminate, this uncertainty by a simple modification of apparatus.

Calculations.—The unit of heat employed, the Calorie, is the quantity required to raise one kilogram of water one degree at the temperature of the experiment. The mean temperature after mixing is calculated by the following formula:

$$T_m = \frac{(A+d)\ T_a + B(T_b - t)}{A+d+B};$$

in which

T_m = mean temperature.

A = water equivalent in grams of solution A in calorimeter.

d = water equivalent in grams of calorimeter, stirrer and thermometer.

B = water equivalent in grams of solution B.

T_a = observed initial temperature of solution A in calorimeter.

T_b = observed initial temperature of solution B in flask.

t = correction in degrees to make the reading of the two thermometers correspond.

The temperatures T_a and T_b, recorded in the tables, are those actually observed. In the calculation of T_m the correction d is used, but no correction is made for difference between the observed zero and the actual zero, as it would not affect the final result. The temperature recorded as T_c is the difference between the calculated mean temperature and the resultant temperature—in other words, the change of temperature due to the reaction—and is positive unless otherwise specified.

The column f in the tables gives the factor by which T_c is multiplied to reduce the heat disturbance of the reaction in Calories to molecular proportions, and H is this final result. The factor f is obtained as follows:

$$f = (A+B+d) \times \frac{\text{mol. wt.}}{\text{grms. taken}} \text{ (of alum).}$$

In all the experiments of this paper the water equivalent of the calorimeter and its belongings is 8.5 grams, while A and B are the volumes in cubic centimeters of the constituent solutions reckoned as grams of water (Berthelot's method of calculation[1]), each numerically equal to 500 cc., unless otherwise specified. $t = .008°$.

Limit of Error.—The reading of temperature is by far the most considerable element limiting the certainty of experimental observation. The quantity of alums used, 20.667 grams, is weighed to one part in more than twenty thousand. The KOH solution is titrated against oxalic acid, and its titration confirmed gravimetrically. The quantity used in an experiment varied from 10.67 cc. to over 200 cc. This was measured in a burette to .05 cc., which would make the maximum variation considerably less than one per cent. of the quantity measured, even when the latter was at its minimum. Whereas, if we put the limit of temperature reading at .005°, and consider that the change in temperature depends upon three separate readings, the maximum of error should be .01°; or .005°, putting the limit of reading at .0025°. This would be a very large per-cent. variation in many of the experiments when the quantity measured falls considerably below 1°. Inspection of the tabulated data will show that in many cases the observed variation of T_c is much smaller than the calculated maximum—*e. g.*, the first six experiments of Table I, where it is only .001°. In most of the experiments a variation of .005° in T_c makes a variation of .24 Cal. in H.

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[1] Essai de Mécanique Chimique **1**, 190.

SERIES I.

The numerical data of these experiments are recorded in Table I. The alum used was the commercial article, well crystallised and free of iron. Of it 20.067 grams were used in each experiment, and the solution prepared as already described. The proportion of water was about 2600 molecules to one of alum; in Thomsen's experiments, 2400. In column h is recorded the rate of heat disturbance per molecule of KOH. The results H and h are seen graphically expressed in Plate I, where x is the number of molecules of KOH added, and y in Line I represents H, in Line III, $h \times 10$.

Inspection of Line I shows that the heat evolution increases with the quantity of KOH, reaching a maximum at $x = 6$ or 6.5, and from this point diminishes until $x = 10$, when the resolution of the precipitate in the excess of KOH is complete. This means that the solution of the precipitate in excess of KOH is accompanied by heat absorption, or is endothermic. It will be shown farther on that the addition of KOH beyond $x = 8.5$ causes no further heat disturbance, and that 8.13 mol. KOH completely redissolve the precipitate; hence, in constructing the line, the value of y at $x = 8.13$ is made the same as at $x = 10$.

Line III reveals still more. It shows a constant rate of heat evolution per molecule of KOH from $x=5$ to $x=1$. At this point it drops abruptly. Now, in the analytical part it will be shown (see Plate II, Line V) that precipitation begins between $x=1$ and $x=1.5$, probably at $x=1.13$. Hence, in constructing Line III the minimum is put hypothetically at $x=1.13$ instead of at $x=1.5$, which is the point actually determined. Inasmuch as the precipitate at first produced redissolves in excess of alum up to $x=1.13$, the drop in the line at this point indicates, probably, that this resolution also is accompanied by heat absorption. This will be evident upon considering that the heat disturbance, h, is a positive resultant, made up of both positive and negative elements. The principal positive element is the formation heat of potassic sulphate, and since this in all probability remains approximately constant for equal portions of KOH entering into combination, it follows that the negative element increases at the point $x=1.13$ in consequence of precipitation. In other words, precipitation is accompanied by heat evolution, and resolution of the precipitate by heat absorption.[1]

Beyond $x=1.13$ there is evidently a tendency to rise slightly up to $x=5$, or thereabouts. The break at $x=4.8$ is within the limit of error, since the larger value recorded in Table I gives the alternative point $x=4.8$ just above the line, as seen in the plate. Indeed, the increase between $x=1.13$ and $x=5$ depends upon differences which lie so close to the limit of experimental error that one must hesitate to consider it more than probable. It would be interesting to establish it beyond doubt, in view of the analytical results shown in Plate II, Line VII. There can be no doubt, however, that the line drops beyond $x=5.12$, as would be expected.

It is to be noted that the maximum in Line I occurs at $x=6$ or 6.5, while in Line III it occurs at $x=5$, which is the point at which the aluminic oxide is completely precipitated. This leads to the question, What causes the continued heat evolution after the precipitation is total? the discussion of which must be deferred until the analytical results have been described. The three experiments recorded in Table III serve, however, to fix one point bearing thereon. 4.8 mol. KOH were added to one of alum in the usual conditions. Then to this mixture were added in the calorimeter the remaining 1.2 mol. KOH, in the proportionate quantity of water, and the heat evolution measured. The results are fairly satisfactory, considering that the necessary conditions of the experiments were not the best for calorimetric measurement. They serve to show, at least, that the continued evolution of heat between $x = 4.8$ and $x = 6$, in Series I, may be accounted for by the action of the 1.2 mol. KOH on the precipitate formed by the 4.8 mol. A previous experiment, made by adding KOH in the calorimeter to the liquid portion of the mixture 1 alum + 5 KOH (the precipitate being removed), gave zero for a result.

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[1] See similar case of lead, Thomsen **1**, 377.

SERIES II.

In the second series of experiments the same quantity of alum was dissolved, 10 mol. KOH added, and the whole made up to 500 cc., as in Series I. To this were added in the calorimeter 500 cc. of sulphuric acid solution containing of H_2SO_4 quantities varying from .5 to 3 molecules. The numerical data are recorded in Table II. It will be seen that the rate of heat disturbance per molecule of H_2SO_4 is practically constant for $n = .5$ and $n = .75$, but increases at $n = 1$; the first precipitation by neutralisation of KOH occurs between $n = .75$ and $n = 1$. The rate then increases to $n = 2.2$, when it again drops. Instead of expressing these direct results graphically, I have calculated from them (at least from Exp. 42–48) the corresponding points in the Lines I and III. The possibility of this calculation will be apparent from considering that *H* in Series II is the formation heat of potassic sulphate plus or minus the heat disturbance involved in separating the equivalent potassic hydrate from whatever form of combination it may be in before the addition of sulphuric acid. If we assume that the n mol. H_2SO_4 (from $n = 1.5$ to $n = 2.2$) are converted into K_2SO_4, and count the formation heat of the latter as a known quantity, we have the means of calculating indirectly the values of y in Series I for $x = 6$, 7 and 10. These values locate the supplementary Lines II and IV, Plate I. They are separated by a small and approximately constant quantity from Lines I and III.

A similar discussion of the values for $n = .5$ and .75 will make evident whether or not the addition of KOH beyond 8.13 mol. has any effect. The formation heat of K_2SO_4 is, according to Thomsen, 31.288 Cal. One-half of this, 15.644 Cal., is larger by .96 than the mean result of Exp. 36–39, Series II, which would indicate that heat was absorbed in liberating KOH from its previous state of combination, and hence that the combination of the 9th and 10th mol. in Series I was accompanied by heat evolution. This, if true, would be an interesting fact; but the question arises, May not the formation heat of K_2SO_4 in Exp. 36–39 be less than 31.288 Cal., this value having been determined for a degree of concentration six times as great? I therefore determined it independently, using first the same quantities of KOH and H_2SO_4 as occur in the reaction $n = .5$, and then six times these quantities, the volume 1000 cc. remaining the same throughout. In the last case, the proportion is about the same as in Thomsen's experiment. The data are shown in Table IV. At the degree of concentration which corresponds to Exp. 36–39, the formation heat of $\frac{1}{2}K_2SO_4$ is found to be (Exp. 57–61) 14.63 Cal., which agrees with H in Exp. 36–39; while for one-sixth this dilution H is found to be 31.26 or 15.63 for $\frac{1}{2}K_2SO_4$; Exps. 53 and 54 correspond to Thomsen's conditions.

This proves that the second half of the 9th mol. and the 10th mol. in Series I are not in chemical combination, or, at least, that there is no evidence of it in the thermal phenomena. In other words, the heat disturbance ceases when 8.13 mol. KOH have been added, as indicated in Line I, Plate I.

As dilution was found to affect the determination of the formation heat of K_2SO_4, it became desirable to test its influence upon the resultant H of Series I, in which this formation heat is the principal element. To do this the reaction heat of 6 mol. KOH on 1 of alum was determined, the absolute amount of substance undergoing change in the standard volume, 1000 cc., being only one-fourth the quantity used in Exp. 23–26, Series I. These data are recorded in Table V. The mean result of the five experiments is 29.26 Cal., in place of 30.66 by the previous experiments.

It seems not improbable, in view of these facts, that the tendency of Line III, Plate I, to rise between $x = 1.5$ and $x = 5.1$ may be due to the increase in the amount of substance undergoing change in the unit of volume.

The complexity of the thermochemical results thus far described made evident the necessity of a sharper definition of the chemical changes actually taking place in the calorimeter. The study of these constitutes the second part of this paper.

PART II.

General Method.—It would seem that the most direct method of obtaining evidence as to the exact chemical change would be to determine the composition of the various precipitates produced in the calorimetric experiments. The impossibility, however, of washing them without changing their composition, indicated rather the analysis of the filtrate from them as the preferable method. Either one determines only the total change in the distribution of constituents between the soluble and insoluble portions of the system.

The method pursued was the following: 50 cc. of alum solution, containing five grams of the crystallised salt, were made up to a little less than 125 cc. The required quantity of KOH solution was also made up to about the same volume. These two solutions were then thoroughly mixed, the volume of the mixture made up accurately to 250 cc. (T 20° C.), again well shaken, and thrown upon a dry filter, the filtration being hastened in some instances by using the pump. From the filtrate separate portions of 50 cc. each were taken, in which were made duplicate determinations of SO_3 and Al_2O_3, and in several instances of K_2O. The SO_3 was determined, of course, by precipitation with $BaCl_2$; the Al_2O_3 by precipitation with NH_3; and the K_2O was weighed as sulphate after the removal of Al_2O_3. The proportion of constituents and water is the same as in the calorimetric experiments, the scale being simply reduced to one-fourth.

Analyses somewhat similar have been made by S. U. Pickering[1] of the precipitates obtained from aluminic sulphate by addition of varying quantities of Na_2CO_3. His method was to determine the SO_3 and Al_2O_3 in the precipitate itself after thorough washing, although he recognised the fact that its composition was changed by the operation. This would be a serious objection to the use of this method for the purposes of this investigation, although less so in his experiments undertaken from a different standpoint. Our results, so far as they cover the same points, do not conflict in the general direction of their indications, although quantitatively they differ somewhat.

Mills also has determined simply the amount of Al_2O_3 precipitated from alum solution by varying quantities of Na_2CO_3.[2]

It should be noted that the method of this investigation gives no evidence as to the degree of hydration of the precipitate: that point I am obliged to pass by.

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[1] Chemical News **45**, 121, 133, 146.

[2] Journal of Chem. Society [2], **41**, 341.

In the first experiment of this series (Exp. *A*) the method was applied in blank to a solution of alum, no KOH being added. The results obtained were:

$$\begin{array}{ll} Al_2O_3 = .1080 \text{ gram.} & SO_3 = .3321 \text{ gram.} \\ \quad = .1074 & \quad = .3326 \\ \hline \text{Mean} = .1077 & \text{Mean} = .3324 \end{array}$$

As these correspond to 1 gram alum taken, multiplying by 100 converts them into per cents. Correcting for the volume of pipettes and flasks makes them respectively 10.90 and 33.64. Adding to these the determinations of K_2O and H_2O, made by separate experiments, makes the complete analysis of the alum used as follows:

	Found.	Cal.
Al_2O_3	10.90	10.76
SO_3	33.64	33.75
K_2O	9.94	9.93
H_2O	45.64	45.56
	100.12	100.00

It is evident that the difference between the results of *A* and of corresponding results of subsequent experiments in which precipitation does occur, gives the amount of Al_2O_3 and SO_3 in the precipitate. The final results of each experiment are reckoned as parts of Al_2O_3 in 100 parts of anhydrous precipitate, and as parts of Al_2O_3 precipitated out of 100 parts of Al_2O_3 present in the total system. The following is an example of a calculation in full:

$$\begin{array}{lr} \quad Al_2O_3. & SO_3. \\ A = .10766 \text{ gram.} & .33231 \\ D = .0689 & .31134 \\ \hline \text{Precipitate} = .03876 & .02097 \end{array}$$

$$\text{Anhydrous precipitate} = \frac{.03876 \times 100}{.03876 + .02097} = 64.89 \text{ per cent. } Al_2O_3.$$

$$Al_2O_3 \text{ of precipitate} = \frac{.03876 \times 100}{.10766} = 36.00 \text{ per cent. of total } Al_2O_3.$$

The data of this series of experiments are recorded in Table VI. The quantity of KOH varies, as will be seen, from 1.5 to 8 molecules.

Before discussing the results, I describe another series made to reverse, as it were, the conditions of the former.

Fifty cc. of alum solution were taken as before, and to these ten molecules KOH added, and the whole made up to a little less than 125 cc. Sulphuric acid solution containing quantities of H_2SO_4 proportional to 1.5, 2, 2.5 and 4 molecules, was added, and the mixture brought accurately to 250 cc. (T 20° C.), thoroughly shaken, filtered, and the filtrate analysed as usual. The only variation was in Exp. T, when 5 mol. HCl were used in place of 2.5 H_2SO_4, and this will be more particularly discussed in a subsequent publication. The data of these experiments are recorded in Table VII.

The calculation of the composition of the precipitate is similar to that in the preceding series, except that account must be taken of the SO_3 added.

In three experiments—viz., H, T, and S''' (in H and T the total amount of precipitate was at its maximum)—the K_2O in the filtrate was determined. The full calculated amount being found, it was deemed unnecessary to determine it at other points, since it evidently formed no part of the precipitate.

Discussion.—The results of the first two series are graphically expressed in Lines V, VI, VII, and VIII, Plate II. In Line V, $x =$ number of molecules of KOH added, and $y =$ per cent. of total Al_2O_3 found in the precipitate; while in Line VII, $x =$ the same, but $y =$ parts of Al_2O_3 in 100 parts of anhydrous precipitate. Continuing Line V beyond $x = 1.5$ and $x = 8$ toward the axis of x, indicates $x = 1.3$ and $x = 8.13$ as the probable points respectively of initial and final precipitation. The line reaches its maximum at $x = 4.8$, making the precipitation of the Al_2O_3 complete at this point.

Line VII shows that the first precipitate is the least basic, containing only 64 per cent. of Al_2O_3; that from $x = 1.5$ to $x = 4$ there is apparently a slight increase of basicity, but that from $x = 4$ to $x = 4.8$ the increase is more rapid; that between $x = 4.8$ and $x = 6$ the rapidity of change is still greater; that at $x = 6$ it drops back again, leaving a precipitate free of SO_3 at $x = 7$. It will be noticed that $x = 4.8$ and $x = 6$ are salient points in these lines, as they are in Lines I and III, expressing the thermal phenomena.

The points in Line VI, $x = 5$, 6 and 7, are obtained from Exp. *N*, *O* and *T* by making x the number of molecules of KOH left unneutralised by the H_2SO_4 added. It will be seen that they approximate closely to the corresponding points in Line V, the difference being probably within the limits of experimental error. This evidently means that when the same amount of free KOH is present, the same precipitate is obtained, whether it come from adding KOH to alum, or from neutralising the excess of KOH in the alkaline solution of Al_2O_3 obtained by adding 10 KOH to alum. This result was unexpected, and suggested at once the possibility of a chemical equilibrium existing between the constituents of the soluble and of the insoluble portions of the system. To test this idea, Exp. *P* was made, using 4 mol. H_2SO_4. Assuming that 4 mol. KOH out of the ten added are uncombined with H_2SO_4, the 4 mol. H_2SO_4 now added would neutralise them, leaving an excess of 2 mol. H_2SO_4, and making a system, neglecting the K_2SO_4, constituted of 1 mol. Al_2O_3 and 2 H_2SO_4, the same which we suppose to exist when 2 mol. KOH are added to 1 mol. alum. Putting $x = 2$, therefore, the results of Exp. *P* give the points *P* in Lines VI and VIII which approach at least the corresponding points in V and VII. Regarding this as a further indication of an equilibrium, I varied the experiment in the following manner (Exp. *Q*): The usual 50 cc. of alum solution were taken, 6 mol. KOH added, and the whole made up to 250 cc. Another portion of 50 cc. alum solution was then taken, and made up to nearly 250 cc. The two solutions thus prepared were then mixed, made up to 500 cc., thoroughly shaken, filtered, and portions of 50 cc. taken from the filtrate for analysis, as usual. The total system here is evidently the same in the proportion of its constituents (water included), as would be obtained by mixing 1 mol. alum and 3 mol. KOH in a volume of 250 cc. At the same time, we can calculate from Exp. *I*, Table VII, what would be the composition of the precipitate, assuming that it remained the same as produced by 6 mol. KOH in the first mixture, increased only by the remaining 9.47 per cent. of the total Al_2O_3 of the first portion; the KOH uncombined with H_2SO_4 in that portion taking SO_3 from the second portion of alum, but causing no increase of precipitate, since it is equivalent to only about .14 mol.

KOH. The precipitate thus calculated would contain 50 per cent. of the total Al_2O_3 of the system, and have a composition of 95.29 per cent. Al_2O_3 to 4.71 per cent. of SO_3. This gives the crossed points *Q* ($x = 3$). But actual analysis of the filtrate gives for the precipitate the results recorded in *Q*, Table VIII, and the points *Q* in Lines VI and VIII. This shows that the initial distribution of constituents between the soluble and insoluble portions of the system has changed completely, approaching that obtained by adding to 1 mol. alum 3 mol. KOH. The change in this case consists only in an increase of SO_3 in the precipitate.

Another experiment was then made (Exp. *R*) by mixing in similar manner (1 alum + 6 KOH) in 250 cc. and (1 alum + 1.5 KOH) in 250 cc.; making a total system equivalent to (1 alum + 3.8 KOH) in 250 cc. Calculating as in *Q*, from Exps. *B* and *I*, the initial composition of this mixed precipitate, and on the assumption that the unneutralised .1 mol. KOH of the 6 mol. KOH is added to the 1.5 mol. in the second portion, we obtain the crossed points *R* ($x = 3.8$). Analysis of the filtrate, on the other hand, gives the points *R* ($x = 3.8$) in Lines VI and VIII, which likewise shows a very considerable change in the precipitate, and a close approach to the system obtained by adding 3.8 mol. KOH to 1 mol. alum. In this case the change is more complex than in *Q*, consisting in the precipitate acquiring both Al_2O_3 and SO_3. In other words, the equilibrium has moved the crossed point *R* up to the point *R* in VI, and the crossed point *R* down to *R* in VIII.

The results already described indicate unmistakably the existence of the equilibrium; but, to vary the evidence still more, Exps. S′, S″ and S‴ were made, as follows:

Aluminum was dissolved in KOH solution and the KOH exactly neutralised by HCl, independent experiments having proved that the precipitate thus obtained is free of acid. The volume of this mixture having the freshly precipitated hydrate in suspension was brought up to 250 cc. Fifty cc. of alum solution (= 5 grams alum) were then added, the whole made up to 500 cc. and thoroughly mixed. Before filtering, portions of 50 cc. each were withdrawn with a pipette, care being taken to insure the uniform distribution of the suspended precipitate by constant stirring. In these portions the precipitate was redissolved by HCl and the total Al_2O_3 of the system determined. The remainder of the mixture was filtered as usual, and portions of 50 cc. of its filtrate taken for the usual determinations of SO_3 and Al_2O_3. The differences between the total Al_2O_3 and SO_3 and the Al_2O_3 and SO_3 found in the filtrate give the composition of the precipitate. In S′ the amount of Al_2O_3 added as precipitate was 1.12 times that added as alum, making a proportion of 2.12 mol. Al_2O_3 to 3 mol. SO_3 in 500 cc. of volume; equivalent to 1 Al_2O_3 and 1.4 SO_3 in approximately 250 cc. This, so far as relation between Al_2O_3 and SO_3 is concerned, should be equivalent to 1 alum $+$ 3.2 KOH. Using, therefore, the analytical results of S′, Table VIII, and making $x = 3.2$, we obtain the dotted points S′, Plate II, approximating closely to the values otherwise obtained; whereas had the precipitate remained unchanged, it would have been 100 per cent. Al_2O_3 and contained 52.82 per cent. of the total Al_2O_3. These values are represented by the crossed points S′. The change consists mainly in acquiring SO_3.

Exp. S″ is similar, the only variation being in the quantity of precipitated Al_2O_3 added. The results are shown in the points S″ ($x = 2.5$); whereas the crossed points S″ indicate what would have been the results had the precipitate remained unchanged. Here, too, the change is in acquiring SO_3.

Still another experiment, S‴, was made, varying again the quantity of Al_2O_3 added. The actual results are shown in the points S‴ ($x = 2$), and the initial precipitate in the crossed points S‴. Here it is apparent that the change consists in gaining SO_3 and losing Al_2O_3.

The proof of equilibrium is indubitable, the initial precipitate gaining or losing Al_2O_3 or SO_3 as may be necessary to bring about the characteristic distribution of constituents for the given conditions. It is also apparent that K_2SO_4 plays no part, and may be considered as practically outside the system, since its presence in quantity varying from less than one molecule to more than ten molecules has not disturbed the leading phenomenon.

Another fact may be noted here. The corresponding points in Lines V, VI, VII and VIII, that lie to the right of $x = 5$, approximate closely, probably within the limits of experimental error. To the left of $x = 5$ the divergence is greatest, but the difference in every instance lies on the side of approach to Lines V and VII from the initial points, never going beyond. The probable explanation of this lies in the fact that, in all the experiments yielding Lines V and VII, also the points of the other lines to the right of $x = 5$, the system in its initial state is homogeneous; while in the remaining experiments, with the single exception of Exp. *P*, it is non-homogeneous (liquid and solid). It is not strange, then, that this non-homogeneity exercises a retarding influence upon the equilibrium. It is rather a matter of surprise that it should not prove more of an obstacle than it does.

EFFECT OF TEMPERATURE, TIME AND DILUTION ON THE EQUILIBRIUM.

Temperature often exerts an influence in reactions such as I have been describing, and to test its effect in this instance is the object of the three following experiments, E′, E″ and E‴. In the first place, two successive experiments were made as nearly alike as possible, in order to measure the probable variation in the final results of a single experiment. I give the details in full. The solutions were prepared in the usual manner, 4 mol. KOH being added to 1 mol. alum. The temperature of the room in both experiments was about 23° C., but the contents of flasks before bringing up to standard volume and before taking out portions of 50 cc. were cooled, as in previous experiments, to 20° C. The results were as follows:

	E′.		*E″.*	
	Al_2O_3.	SO_3.	Al_2O_3.	SO_3.
Found in 50 cc. I =	.0174 gram.	.28221	.0159	.28203
II =	.0174	.28210	.0162	.28190
Mean =	.0174	.28216	.0161	.28197

	E′.		*E″.*	
	Al_2O_3.	SO_3.	Al_2O_3.	SO_3.
A =	.10766 gram.	.33231	.10766	.33231
E′ =	.0174	.28216	.0161	.28197
Precipitate =	.09026	.05015	.09156	.05034

	E′.	*E″.*
Anhydrous precipitate =	64.28 per cent. Al_2O_3	64.52 per cent. Al_2O_3
=	35.72 per cent. SO_3	35.48 per cent. SO_3
Precipitate =	83.84 per cent. of total Al_2O_3	85.05 per cent. of total Al_2O_3.

It will be seen that the SO_3 determinations do not differ appreciably more than the duplicate determinations of SO_3 in the same solution; while the amounts of Al_2O_3 obtained differ by more than a milligram, one part in seventeen. So in another instance, .2893 and .2899 gram SO_3 were obtained in two experiments entirely distinct from the beginning. It would almost seem that the equilibrium was more sharply defined with reference to SO_3 than to Al_2O_3. Yet it should be borne in mind that the amounts of SO_3 actually weighed are always large, .28 gram or more, while the amounts of Al_2O_3 weighed were as low as .01 gram, and hence the experimental determination of SO_3 is less affected by error than that of Al_2O_3.

The final results being dependent on the ratio between differences, small compared with the quantities actually measured, considerable latitude of variation must be allowed.

The experiment was then repeated, E''', the only variation being that, after the flask was filled to 250 cc. (at 21° C.), it was heated to about 50–55° C. for twenty-five minutes, then turned into a large beaker with glass cover and heated fifteen minutes more, and finally boiled two or three minutes. The liquid on the cover was rinsed off with the solution, and the whole thrown while boiling hot upon a dry filter, which was covered during the ten minutes of filtration. The filtrate was then cooled to 20° C., and portions of 50 cc. taken as usual for analysis. The loss of water by evaporation could not have been great, and would not affect the ratio between Al_2O_3 and SO_3. The results were:

	Al_2O_3.	SO_3.
I =	.0148	.30473
II =	.0148	
Mean =	.0148	.30473

This makes a precipitate containing 86.25 per cent. of the total Al_2O_3, with a composition of 77.10 per cent. Al_2O_3 and 22.90 per cent. SO_3. The precipitate at the temperature of boiling has, therefore, lost considerable SO_3, while the ratio of the Al_2O_3 precipitated to the total has not much changed.

Exp. E^{IV}. A second variation was made to test the influence of dilution on the equilibrium, since many of the experiments already described indicate that water plays a part in the reaction besides that of a mere solvent. Alum and KOH in the same quantity as in E', E'' and E''' were mixed, and the solution made up to 1000 cc., instead of 250, making the absolute quantity in unit of volume one-fourth what it was in the preceding experiments. Of the filtrate, portions of 100 cc. were taken, instead of 50, and the quantities of SO_3 and Al_2O_3 found were multiplied by two in order to make them comparable with the others. The results were:

	Al_2O_3.	SO_3.
I =	.0162	.28570
II =	.0160	.28578
Mean =	.0161	.28574

This indicates a precipitate containing 85.05 per cent. of total Al_2O_3, and of composition 66.29 per cent. Al_2O_3 and 33.71 per cent. SO_3.

Dilution also has tended to diminish SO_3 in the precipitate without changing the proportion of Al_2O_3 precipitated.

Is the equilibrium a function of time also? To answer this, a mixture was prepared (Exp. E^{v}) at the same time as E', and in precisely the same manner. But, instead of filtering at once, as in E', the mixture was allowed to stand in a closed flask at the temperature of the room for seven days, and then filtered as in E', and the filtrate analysed. The result was:

	Al_2O_3.	SO_3.
I =	.0152	.28210
II =	.0146	.28217
Mean =	.0149	.28214

This makes a precipitate containing 86.12 per cent. of the total Al_2O_3, and in composition 64.89 per cent. Al_2O_3 and 35.11 per cent. SO_3, or practically the same as in E'. Here, too, is to be seen the close agreement in quantity of SO_3 and the greater variation in Al_2O_3.

This experiment was suggested by the fact that the basic filtrates obtained by adding one or more molecules of KOH, and removing the precipitate, yield a second precipitate on standing, the length of time apparently depending on the degree of basicity. This second precipitate is also produced in a few minutes by boiling, or by adding a considerable quantity of water. Exp. E^{v} is therefore interesting as showing that time does not affect the equilibrium while the original precipitate remains in the system.

CONCLUSION.

It is clear, from the evidence herein set forth, that in the reaction which has been the subject of investigation we have another instance of chemical equilibrium or mass reaction, and the question at once arises, What is the cause of it? Without attempting to answer this definitely at present, we suggest the probability that it may be due to the progressive dissociation by water of basic compounds of Al_2O_3 and SO_3 on the one hand, and of potassic aluminate on the other. It would appear from Exps. S', S'' and S''', that $Al_2O_3 . 3 SO_3$ must itself be partly dissociated in water solution, and it is not improbable that the matter may be still further complicated by the dissociation of another substance formed from the products of decomposition of the first. I hope to obtain definite evidence upon this point, by continuing a line of investigation already begun. That the basic sulphates of alumina are dissociated, is apparently indicated by the fact already cited, that the filtrates in experiments B to H yield a second precipitate on heating, diluting, or standing some length of time; while the crystallised potassic aluminate to which Fremy assigns the formula, $K_2O . Al_2O_3 . 3H_2O$, decomposes on the addition of water with the separation of aluminic hydrate.

However that may be, it is evident—(1), that the reaction between alum and KOH is not by any means as represented in what may be called the ideal equation cited in the beginning of this paper, but that it is much complicated by secondary reactions which render it entirely unsuitable for the determination of the formation heat of the sulphate and other compounds of alumina, although the numerical error introduced by its use may not be great; and (2), that these secondary reactions are of the nature of chemical equilibriums or mass reactions, the distribution of the constituents of the system about the line of solubility being a function of temperature, volume (*i. e.*, dilution), and total mass of constituents.

TABLE I.

1 Alum + n KOH.

$A = B = 500$. $d = 8.5$. $f = 47655.4$.

No. of Exp.	n.	T_a.	T_b.	T_m.	T_c.	$H = T_c \times f$.	$h = H \div n$.	Mean H.	Mean h.
		°	°	°	°	Cal.	Cal.	Cal.	Cal.
1	0.5	16.66	17.275	16.96	.060	2.86	5.72	2.85	5.69
2	0.5	16.4575	17.2225	16.833	.0595	2.84	5.67		
3	1.0	16.6675	17.2925	16.973	.1195	5.70	5.70	5.72	5.72
4	1.0	16.57	17.52	17.037	.1205	5.74	5.74		
5	1.5	16.70	17.0675	16.878	.1695	8.08	5.39	8.09	5.39
6	1.5	16.826	17.73	17.27	.1700	8.10	5.40		
7	2.5	17.02	18.073	17.538	.287	13.68	5.47	13.58	5.43
8	2.5	16.6075	17.04	16.818	.283	13.49	5.39		
9	2.5	16.545	17.40	16.965	.285	13.58	5.43		
10	4.5	17.08	17.93	17.497	.513	24.45	5.43	24.42	5.43
11	4.5	16.525	17.16	16.836	.514	24.50	5.44		
12	4.5	17.44	18.255	17.84	.510	24.31	5.40		
13	4.8	16.18	17.0525	16.609	.5335	25.42	5.30	25.79	5.37
14	4.8	17.2125	17.845	17.522	.548	26.12	5.44		
15	4.8	17.37	18.5775	17.965	.535	25.50	5.31		
16	4.8	16.4325	17.80	17.107	.548	26.12	5.44		
17	5.12	17.03	16.92	16.971	.594	28.31	5.53	28.39	5.55
18	5.12	17.06	17.68	17.363	.5945	28.33	5.53		
19	5.12	16.78	17.75	17.257	.5955	28.38	5.54		
20	5.12	16.17	17.0075	16.581	.599	28.55	5.58		
21	5.5	16.69	17.46	17.068	.632	30.12	5.48	30.14	5.48
22	5.5	16.49	17.35	16.912	.633	30.17	5.49		
23	6.0	19.5825	20.15	19.86	.640	30.49	5.08	30.66	5.11
24	6.0	19.84	20.5075	20.167	.633	30.17	5.03		
25	6.0	16.66	17.84	17.241	.6515	31.05	5.18		
26	6.0	16.6925	17.62	17.148	.6495	30.95	5.16		
27	6.5	16.2375	16.8825	16.553	.647	30.83	4.74	30.83	4.74
28	6.5	16.62	17.895	17.248	.6495	30.95	4.76		
29	6.5	16.445	17.705	17.066	.644	30.69	4.72		
30	7.0	19.15	19.72	19.429	.621	29.59	4.23	29.59	4.23
31	10.0	16.9725	18.01	17.483	.617	29.40	2.94	29.27	2.93
32	10.0	16.46	17.84	17.14	.610	29.07	2.91		
33	10.0	16.62	17.74	17.171	.619	29.50	2.95		
34	10.0	19.26	20.34	19.791	.6115	29.14	2.91		
35	10.0	19.1975	20.21	19.696	……..	29.22	2.92		

TABLE II.

1 Alum + 10 KOH + n H_2SO_4.

$A = B = 500$. $d = 8.5$. $f = 47655.4$.

No. of Exp.	n.	T_a.	T_b.	T_m	T_c.	$H = T_c \times f$.	$h = H \div n$.	Mean H.	Mean h.
		°	°	°	°	Cal.	Cal.	Cal.	Cal.
36	.50	19.2575	20.49	19.865	.305	14.54	29.07	14.68	29.36
37	.50	19.41	20.445	19.919	.311	14.82	29.64		
38	.75	17.81	19.14	18.465	.4575	21.80	29.07	21.83	29.10
39	.75	17.8175	19.0075	18.404	.4585	21.85	29.13		
40	1.00	18.19	19.5525	18.862	.628	29.93	29.93	30.05	30.05
41	1.00	18.21	19.725	18.957	.633	30.17	30.17		
42	1.50	17.92	18.305	18.107	.998	47.56	31.71	47.39	31.60
43	1.50	17.9675	18.9375	18.444	.991	47.23	31.49		
44	2.00	17.8975	18.98	18.43	1.340	63.86	31.93	63.55	31.77
45	2.00	19.094	19.65	19.366	1.3415	63.93	31.97		
46	2.00	17.605	19.0375	18.311	1.319	62.86	31.43		
47	2.20	17.82	19.0575	18.43	1.4575	69.46	31.57	69.28	31.49
48	2.20	18.22	18.53	18.37	1.450	69.10	31.41		
49	3.00	17.80	18.665	18.225	1.785	85.07	28.36	85.07	28.36

TABLE III.

(1 Alum + 4.8 KOH) + 1.2 KOH.

$A + d = 1008.5$. $B = 124.96$. $f = 47655.4$.

No. of Exp.	T_a.	T_b.	T_m.	T_c.	$H = T_c \times f$.	Mean H.
	°	°	°	°	Cal.	Cal.
50	18.08	18.67	18.144	.086	4.10	3.83
51	17.57	17.87	17.602	.073	3.48	
52	17.0475	16.565	16.993	.082	3.91	

TABLE IV.

$2\,KOH + H_2SO_4$. $A = B = 500$. $d = 8.5$.

No. of Exp.	n = grams of H_2SO_4.	T_a.	T_b.	T_m.	T_c.	$H = \frac{T_c \times 1008.5 \times 98.}{n = \text{gram } H_2SO_4.}$	Mean H.
		°	°	°	°	Cal.	Cal.
53	6.8071	17.6925	18.45	18.064	2.1435	31.12	31.26
54	6.8071	17.64	18.9075	18.264	2.1385	31.05	
55	6.227	14.62	15.43	15.018	1.9895	31.58	
56	6.227	15.27	15.96	15.608	1.972	31.30	
57	1.0391	17.1725	19.1275	18.138	.312	29.43	29.26.
58	1.0391	18.30	19.45	18.866	.3065	28.91	
59	1.024	14.1675	14.8950	14.524	.311	29.76	
60	1.024	14.845	15.485	15.158	.307	29.38	
61	1.024	14.31	15.6275	14.959	.301	28.81	

TABLE V.

1 Alum + 6 KOH. $A = B = 500$. $d = 8.5$.

No. of Exp.	T_a.	T_b.	T_m.	T_c.	$H = \frac{T_c \times 1008.5 \times 948.24.}{5}$	Mean H.
	°	°	°	°	Cal.	Cal.
62	18.76	19.83	19.287	.1505	28.82	29.26
63	19.01	20.07	19.532	.148	28.34	
64	19.13	19.77	19.443	.157	30.06	
65	19.54	19.9075	19.718	.152	29.10	
66	19.9925	20.22	20.101	.1565	29.96	

TABLE VI.—Analyses.

1 Alum + x KOH.

Exp.	x.	Grams Al_2O_3 found in 50 cc. of filtrate.	Grams SO_3 found in 50 cc. of filtrate.	Al_2O_3 in 100 pts. of prec.	SO_3 in 100 pts. of prec.	K_2O in 100 pts. of prec.	Per cent. of total Al_2O_3 in prec.
A	0.	.10766	.33231	0.	0.	0.	0.
B	1.5	.09738	.32651	63.93	36.07	......	9.55
C	2.0	.08310	.31883	64.56	35.44	......	22.81
D	2.5	.0689	.31134	64.89	35.11	......	36.00
E	4.0	.01995	.28588	65.39	34.61	......	81.47
H	4.79	.0	.28967	71.63	28.37	0.	100.
I	6.0	.0102	.32699	94.82	5.18	......	90.53
J	6.5	.0294	.32827	96.26	3.74	......	72.69
K	7.0	.0547	.33174	100.	0.	......	49.19
L	8.0	.1019	.33231	100.	0.	......	5.35

TABLE VII.—ANALYSES.

(1 Alum $+ 10$ KOH) $+ x$ H_2SO_4.

Exp.	*x*.	Grm. Al_2O_3 found in 50 cc. of filtrate.	Grm. SO_3 found in 50 cc. of filtrate.	Al_2O_3 in 100 pts. of prec.	SO_3 in 100 pts. of prec.	K_2O in 100 pts. of prec.	Per cent. of total Al_2O_3 in prec.
N	1.5	.0540	.45788 cal. .45679 found.	100.	0.	......	49.84
O	2.0	.0119	.50011 cal. .49673 found.	96.59	3.41	......	88.95
T	2.5	.0	.33231 cal. .29512 found.	74.33	25.67	0.	100.
P	4.0	.0867	.66969 cal. .66036 found.	69.20	30.80	......	19.47

TABLE VIII.—ANALYSES.

1 Alum $+ x$ KOH.

Exp.	*x*.	Grm. Al_2O_3 found in 50 cc. of filtrate.	Grm. SO_3 found in 50 cc. of filtrate.	Al_2O_3 in 100 pts. of prec.	SO_3 in 100 pts. of prec.	K_2O in 100 pts. of prec.	Per cent. of total Al_2O_3 in prec.
Q	3.0	.0547	.30898	69.42	30.58	......	49.19
R	3.8	.0300	.29598	68.13	31.87	......	72.13
S′	3.2	.0516	.13951	70.11	29.89	......	54.78
S″	2.5	.0543	.15017	70.33	29.67	......	41.11
S‴	2.0	.0608	.15835	71.74	28.26	0.	24.57

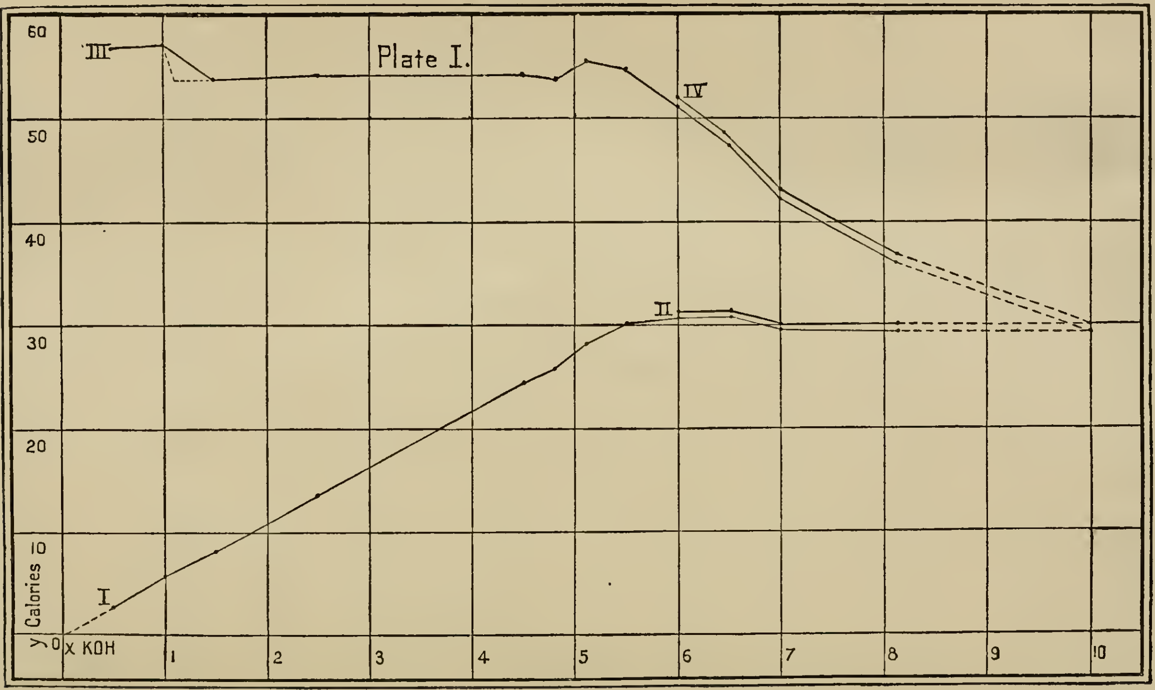
Plate I.
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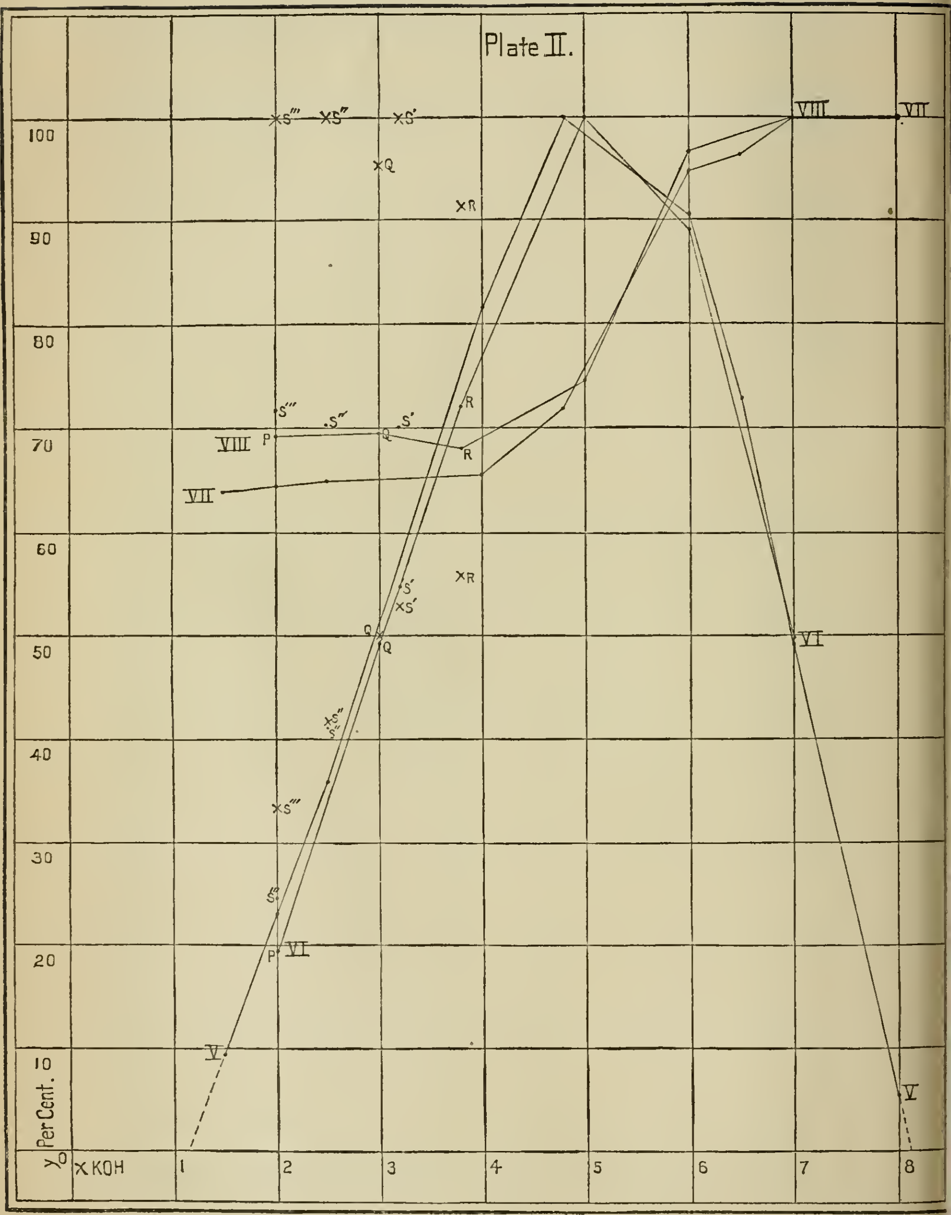

Plate II.
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V

COMPOSITION AND RELATIVE DIGESTIBILITY OF FEEDING-STUFFS.

By E. F. Ladd.

The chemical composition of American feeding-stuffs has, through the efforts of experiment stations and agricultural colleges, been quite thoroughly investigated. But chemical analysis reveals to us only the composition of the fodder—its potency, and not its nutritive value, which can only be known by a knowledge of its digestibility. The mere fact that two substances have nearly the same chemical composition will not warrant us in assuming that they are of like value for feeding. We must know the ease and efficiency of digestibility as well as the chemical composition.

The abundance of natural foods, and the difficulty and expense of experiments for determining the digestibility, have prevented our gaining any extensive knowledge of this subject in America.

Several attempts have been made to determine, by artificial digestion, the nutritive value. Stutzer[1] proposed to determine the digestibility of the albuminoids—the most important compound—by means of the gastric fluid prepared from a hog's stomach, but this is a difficult and tedious task, and not without its faults.

Appreciating the necessity for a better knowledge of American feeds, I set to work analysing and testing their digestibility by the different methods. After much study, and experimenting with Stutzer's method, I instituted a series of experiments, with a solution from scale pepsin as a digestive menstruum, which gave results far above any expectation.

The work accomplished may be found in the Report of the New York Agricultural Experiment Station for 1885; hence, I will only give here a *résumé* of the essential features, with tables of results and a brief consideration of the same.

The Pepsin Method.

A muriatic-acid solution of 0.2 per cent. was prepared and to each litre were added 5 grams of pepsin.[2] Fresh solutions were made for each test. The substance to be digested was thoroughly comminuted as for a chemical analysis. One or two grams were taken, according to richness in nitrogen.

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[1] Journal für Landwirthschaft, 1880, p. 195; also Report of Maine State College, 1883.

[2] Scale pepsin from Henry Thayer & Co.

The substance was placed in an Erlenmeyer flask and 150 cc. of the pepsin solution added. Once in two hours 0.1 gram of HCl was added until the solution contained 0.7 gram. The flasks were set in a water-bath heated at from 38° to 42° C. for 14 hours, then allowed to cool down during the night, and on the following day the heating was continued for six hours. They were then filtered, thoroughly washed with water until free from any traces of acid, then with alcohol, and the contents of the filter transferred to a nitrogen flask and dried at 100° C.

The nitrogen in the undigested residue was then determined by Kjeldahl's method.

In Table I are given the analyses of the substances examined. The analyses are given for both dry substances and calculated to actual water contents, but the digestion coefficients are given for the dry substances only.

Tables II and III give the results obtained from the experiments.

In this article the term crude albuminoids applies to N × 6.25, and the true albuminoids were determined by Stutzer's cupric-hydrate method.

Digestion coefficients are given for both crude albuminoids and the true albuminoids.

NOTES ON TABLE I.

The first three hays were from the same lot. No. 1[1] as harvested, and in good condition. No. 2 was a sample of the same spread on the ground for one month, exposed to the weather, and selected as an average sample. No. 3 was a sample of the poorest, selected from No. 2, and was somewhat decayed.

No. 4. This was like No. 1, but gave slightly more nitrogen.

No. 5. A portion of No. 4 after having been prepared for analysis, then steamed and redried.

Nos. 13 and 15 were waste products from the American Glucose Co.

No. 14. A similar product from the Glen Cove Starch Co.

Nos. 18 and 19. Selected as fair representatives of the old- and new-process linseed meals.

No. 24. The pea meal used in this test was a sample from the meal fed the cows of Mr. Bronson during the butter test in June, 1885.

No. 22. A sample of corn meal fresh from the mill.

[1] Bulletin No. 6, N. Y. Agl. Exp't Station.

No. 23. Same as No. 22, cooked by boiling with water, then dried and examined.

No. 27. Sample of corn meal having lain in bin fully three months.

No. 28. Same as last, treated as No. 23.

No. 30. No. 29 after remaining in bin until badly heated and somewhat mouldy.

The determinations have all been made in duplicate and only the average given in the following tables.

TABLE No. I.

		FRESH SUBSTANCES.						DRY SUBSTANCES.				
	HAY AND COARSE FODDERS.	Water.	Albuminoids N X 6.25.	Crude fibre.	Nitrogen, free extract.	Fat, ether extract.	Ash.	Albuminoids.	Crude fibre.	Nitrogen, free extract.	Fat, ether extract.	Ash.
1	Clover hay	14.53	11.80	28.22	35.84	3.31	6.30	13.812	33.025	42.113	3.865	7.185
2	Same exposed, average	14.53	10.42	35.14	33.28	2.48	4.15	12.187	41.110	38.953	2.900	4.850
3	Same exposed, poorest	14.53	11.73	34.79	31.79	2.52	4.64	13.843	40.710	37.057	2.960	5.430
4	Clover hay	....	....	....	....	....	....	14 531	...	....	3.86	....
5	Same steamed	....	....	....	....	...	....	14.343	....	....	3.41	....
6	Hay, ordinary, mixed	15 22	5.14	31.28	41.36	2.06	4.94	5.94	36.89	48.91	2.43	5.83
7	Hay, poor, many daisies	16.85	4.94	35.89	35.58	2.08	4.66	5 94	43.16	42.80	2.50	5.60
8	Fodder corn	56 49	3.40	15.46	20.64	1 30	2.71	7.81	35.54	47.44	2.98	6.23
9	Soja hispida	21.23	8.42	22.34	38.29	1.35	8.37	10 69	28.35	48.59	1.75	10.62
10	Ensilage	84.58	1.13	5.01	7.22	1.15	.91	7.31	32 48	46.84	7.45	5.92
	BY-PRODUCTS.											
11	Wheat bran	13.72	13.69	10.52	53.09	2.86	6.12	15.87	12.19	61.53	3.32	7.09
12	Ship stuff	16.00	14.96	4 71	54.12	3.99	6.32	17.81	5.68	64 12	4.87	7.52
13	Gluten meal	8.25	30.16	2.78	52.79	5.16	.86	32 87	3.03	57.54	5.62	.94
14	Starch refuse	63.60	7.66	3.68	20.78	4.04	.24	21.06	10.10	57.08	11.11	.65
15	Starch feed	6.00	16.04	13.02	58.14	6.08	.72	12.50	12.43	65.11	9.45	.51
16	Corn feed, ground germ	8.35	9.85	5.76	62.91	11.21	1.92	10.75	6.28	68.64	12.23	2.10
17	Corn feed, ground hull	6.12	7.04	13.26	64.55	7.53	1.50	7.50	14.12	68.76	8.02	1.60
18	Linseed meal, old process.	8.07	31.71	12.31	34.38	8.20	5.33	34 50	13.39	37.40	8.92	5.79
19	Linseed meal, new process.	8.55	32.35	13.77	38.13	2.13	5.07	35.37	15.06	41.70	2.33	5.54
20	Cotton-seed meal	18.52	35.21	5.74	21.66	12.32	6.55	43.21	7.31	26.32	15.12	8 04
21	Same cooked	18.52	34.82	....	....	...	....	42 73	....	...	....	....
	GRAINS.											
22	Corn meal	12.21	10.86	2.24	68.23	5.06	1.40	12 37	2 55	77.78	5.77	1.59
3	Same cooked	12.21	9.88	2.90	69.77	3.85	1.39	11.25	3 31	70.48	4.38	1.58
4	Pea meal	12.08	21.37	11.06	52.02	.86	2.61	24.31	12.58	59.17	.97	2.97
5	Crushed oats	10 09	11.63	16.57	53.98	4.49	3.24	11.87	22 33	58.51	3.90	3.39
6	Corn meal	24.54	8.20	1.52	60.60	3.96	1.18	10.87	2.02	80 31	5.24	1.56
7	Corn meal	8.01	9.61	2.14	73.80	4.98	1.47	10.41	2.33	80.35	5 41	1.50
8	Same cooked	8.01	9.09	2.27	75.80	3.52	1.31	9 87	2.47	82.39	3.85	1.42
9	Corn meal	15.80	10.31	1.58	67.64	3.62	1.05	12.25	1.88	80.33	4.30	1.24
0	Same heated in bin	15.80	9.99	3.88	67.42	1.44	1.57	11.87	4.61	79.93	1.71	1.87
1	Wheat, Clawson's winter.	12.80	13.00	3.76	67 40	1.64	1.40	14.93	4.31	77.28	1.88	1.60
2	Bean, navy or pea	12.39	22.17	7.21	53.14	1.38	3.71	25.31	8.23	60.66	1.57	4.23

TABLE No. II.

Digested by Fluid from Hog's Stomach.

No. corresponding to No. of analyses.		Per cent. of crude albuminoids N × 6.25.	Per cent. of true albuminoids.	Per cent. undigested.	Per cent. of crude albuminoids digested.	Per cent. of true albuminoids digested.
1	Clover hay...........................	13.81	10.03	3.62	73.75	63.91
2	Same exposed, average..............	12.19	9.38	6.20	49.23	33.90
3	Same exposed, poorest.............	13.84	11.31	7.09	48.76	37.31
26	Corn meal..............................	10.87	8.31	1.71	83.98	79.42
10	Ensilage................................	7.31	4.46	2.32	68.20	47.98

TABLE No. III.

Digested by Pepsin Solution.

No. corresponding to No. of analyses.	Hay and Coarse Fodders.	Per cent. of crude albuminoids N × 6.25.	Per cent. of true albuminoids.	Per cent. undigested.	Per cent. of crude albuminoids digested.	Per cent. of true albuminoids digested.
4	Clover hay...........................	14.53	10.03	4.70	67.65	53.14
5	Same steamed.........................	14.34	...	6.70	53.27	...
6	Hay, ordinary, mixed..............	5.94	...	2.09	35.32	...
7	Hay, poor quality, many daisies.	5.94	5.44	2.51	57.69	53.86
8	Fodder corn..........................	7.81	5.88	2.89	63.00	50.83
9	Soja hispida..........................	10.68	9.56	2.57	75.92	73.11
10	Ensilage................................	7.31	4.56	2.82	61.35	39.25
	By-Products.					
11	Wheat bran............................	15.87	13.00	2.65	83.27	79.61
13	Gluten meal...........................	32.87	...	5.51	83.23	...
14	Starch refuse.........................	21.06	...	5.60	73.43	...
15	Starch feed............................	12.50	12.68	4.89	60.80	61.36
16	Corn feed, ground germ............	10.75	...	4.54	57.98	...
17	Corn feed, ground hull..............	7.50	...	2.28	69.71	...
18	Linseed meal, old process	34.50	33.13	3.61	89.52	89.10
19	Linseed meal, new process........	35.37	32.19	7.62	78.44	76.33
20	Cotton-seed meal.....................	43.21	40.25	5.30	87.73	86.83
21	Same cooked..........................	42.73	...	11.19	73.81	...
21	Ship stuff..............................	17.81	16.81	2.34	87.86	86.08
	Grains.					
24	Pea meal................................	24.31	20.19	2.75	88.69	86.38
25	Crushed oats..........................	11.87	10.31	2.15	81.89	79.14
26	Corn meal..............................	10.87	8.31	1.50	86.15	81.95
27	Corn meal..............................	10.41	7.64	2.85	72.58	64.00
28	Same cooked..........................	9.87	7.61	3.64	63.16	52.17
31	Wheat, Clawson's winter...........	14.93	8.81	1.93	87.07	78.09
29	Corn meal..............................	12.25	8.81	3.57	70.85	59.48
30	Same heated..........................	11.81	8.81	3.58	69.79	59.35
22	Corn meal..............................	12.37	9.41	3.87	68.63	58.87
23	Same cooked..........................	11.25	5.19	4.44	60.53	16.37
32	Bean, navy or pea...................	25.31	22.06	1.13	95.59	94.93

Of the feeds examined in per cent. of digestibility of the albuminoids, bean meal stands the highest, linseed meal (old process) next, and pea meal but little less, while the mixed hay of rather inferior quality, but similar to much hay fed, stands lowest. The old-process linseed meal shows a higher per cent. of digestibility than the new-process: this difference is due, very likely, to the partial cooking of the meal by steam during the process of oil extraction and preparation of the meal for feed. Cotton-seed meal, much the richest substance examined, gives a high coefficient for digestibility. A marked difference exists between the first three hays, showing plainly the difference between well-cured hay and that exposed to the weather.

Of the raw and cooked foods examined, in every instance the higher digestion coefficients were obtained for the raw foods, and an examination of the table of analyses shows an actual loss in albuminoids by cooking, and a change in the fat rendering it insoluble in ether, and unacted upon by acids or alkalies of the strength used for fibre determinations.

REVIEWS AND REPORTS.

An Account of Recent Researches on Thiophene and its Derivatives.

In December, 1882, Victor Meyer[1] called attention to the fact that there is a difference between the chemical conduct of the purest benzene from coal tar and that from benzoic acid; that while that from coal tar, as shown by Baeyer[2] in 1879, is capable of reacting, in the presence of strong sulphuric acid, upon isatin to form indophenin according to the following equation, as given at that time:

$$C_8H_5NO_2 + C_6H_6 = H_2O + C_{20}H_{15}NO,$$

that from benzoic acid effects, under similar conditions, no such change. Meyer forthwith undertook a study of the cause of this difference between these benzenes of different origin. Of a number of hypotheses made at the outset as to the cause in question, the following one soon proved to be correct—namely, that coal-tar benzene contains two bodies, physically and chemically very similar, one of which is more susceptible to chemical change than the other, and is capable of combining with isatin; when treated with strong sulphuric acid it is converted into the sulphonic acid, while the less susceptible body is unaffected. Coal-tar benzene,[1] when shaken for some time with concentrated sulphuric acid, loses its power of reacting with isatin as described, but the sulphonic acid thus formed, when subjected to dry distillation, gives rise again to benzene, which is active toward isatin.

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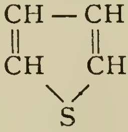
[1] V. Meyer, Berichte der deutschen chemischen Gesellschaft **15**, 2893. [2] *Ibid.* **12**, 1311.

This fact suggested a method of isolating this new substance so intimately associated with coal-tar benzene. A large quantity, 250 litres, of the purest commercial benzene was vigorously shaken for four hours with 25 litres of strong sulphuric acid; the resulting acid product was neutralised with lead carbonate and then the lead salt, mixed with one-fourth its weight of ammonium chloride, subjected to dry distillation. The product of this distillation contained 70 per cent. of the new body and 30 per cent. benzene. The new substance is obtained pure by again treating the above raw product, diluted with 100 times its volume of ligroin, with strong sulphuric acid, which now does not attack the benzene, and subsequently distilling the lead salt mixed as before with ammonium chloride. This method produces the new substance chemically pure. Thus obtained it forms a colorless, extremely mobile oil, boiling-point 84° (corr.). Analysis established the formula C_4H_4S, which is also in accordance with a determination of its vapor density. Strong sulphuric acid dissolves it in the cold with the greatest ease, but also destroys it completely; hence the necessity of diluting the raw product with an indifferent oil such as ligroin. This conduct towards sulphuric acid and the indophenin reaction with isatin serve as means to detect and identify it. Commercial benzene contains 0.5 per cent. of this substance.

To this new compound Meyer[2] gave the name "thiophene," which shows the presence in it of sulphur, and at the same time indicates the striking similarity which exists between it and its derivatives to the phenyl compounds. The study of a few derivatives, such as the bromine substitution products, the sulphonic acid, amide and chloride, and the carbonic acid, developed the idea that this body must be constituted similarly to benzene, and its structure is represented by the following scheme, in which a bivalent sulphur atom takes the place of two CH groups; thus:



This structure admits the possibility also that thiophene is fur-

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[1] V. Meyer, Berichte der deutschen chemischen Gesellschaft **16**, 1465. [2] *Ibid.* **16**, 1470.

furan C_4H_4O, in which oxygen is replaced by sulphur. The analogy in structure of thiophene, furfuran and pyrrol will be discussed further on in connection with a consideration of certain parallel syntheses of these three bodies.

General Transformations.

Although but a short time has elapsed since the isolation of thiophene, a great many derivatives have been prepared and studied. The rapidity with which these bodies have appeared is not strange, in view not only of the active investigation prosecuted in this extensive and interesting field, but also of the fact that, owing to the great similarity between the thiophene and the benzene series, a number of important general transformations carried out in connection with the latter series have been found equally applicable to thiophene and its homologues.

Quite a long list of chlorine, bromine, iodine, nitro and sulpho derivatives are well known. Perhaps the most important general statements that can be made in regard to them are, in the first place, that they show, with scarcely any exceptions, the indophenin and the Laubenheimer[1] reactions; secondly, they have a surprisingly strong resemblance to the corresponding compounds of the benzene series (this likeness being in some cases so perfect that analysis or the indophenin reaction only will serve as distinguishing means); lastly, they are prepared usually in the same general manner as the analogous benzene compounds.

The chlorine[2] and bromine[3] substitution products are the ready result of treating raw thiophene directly with these elements; the iodine[4] compounds are formed by the action of iodine and mercuric oxide upon crude thiophene. Strong sulphuric acid acts destructively upon undiluted thiophene, but gives rise to well-crystallising and attractive sulphonic acids when its action is modified by dilution with benzene or ligroin.

Concentrated nitric acid[5] acts with destructive and even explosive violence upon pure thiophene; the presence of a negative atom or group in thiophene seems, however, to make it more stable towards oxidising agents and more susceptible to nitration.

Thus iodo-thiophene, by slow and careful treatment with nitric acid, is converted into the iodo-nitro derivative. Also, dibromthiophene is readily transformed into nitro derivatives with less violent action than the iodine product. A great many attempts to obtain nitro-thiophene by the direct action of nitric acid upon pure and also upon diluted thiophene were made in vain, until at last success[6] was attained by passing air laden with thiophene vapor through fuming nitric acid; in this manner mono-nitro- and two isomeric dinitro-thiophenes were prepared. These dinitro compounds are of particular interest because of the fact that the one melting at the lower point (52°) is transformed, by repeated distillation with water vapor, into the other, which melts at 78°. The lower melting body retains its melting-point even after extensive fractional crystallisation from alcohol, thus indicating that it is a distinct substance.

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[1] V. Meyer, Berichte der deutschen chemischen Gesellschaft **8**, 224. [2] L. Weitz, *ibid.* **17**, 794. [3] *Ibid.* **16**, 1465. [4] Meyer and Dyson, *ibid.* **17**, 1558. [5] H. Kreis, **17**, 2073. [6] V. Meyer and O. Stadler, *ibid.* **17**, 2648.

The reduction[1] of nitro-thiophene to the amido compound offered unexpected difficulties, since it is either entirely unaffected or is decomposed by the action of the reducing agents ordinarily used for this purpose. Success was finally attained, after many vain attempts, by the use of tin and hydrochloric acid in dilute alcoholic solution. The tin double salt $\left.\begin{matrix} C_4H_3SNH_2,HCl \\ C_4H_3SNH_2,HCl \end{matrix}\right\} + SnCl_4$ is by this means obtained, but the free base, thiophenine (amido-thiophene) itself is an exceedingly subtile body which can readily be lost by decomposition, is liable to be overlooked altogether, and is preserved unchanged only by exercise of the greatest care.

The Friedel and Crafts reaction,[2] of such great importance in the aromatic series, is equally applicable to the thiophene series; in the case of thiophene it is unnecessary to use the pure substance, since thiophene is acted upon more readily than benzene; hence crude thiophene (60 per cent. thiophene and 40 per cent. benzene) is employed. By means of this reaction, performed in the usual manner, such interesting bodies as the following have been produced: Phenyl-thienyl-ketone, $C_6H_5-CO-C_4H_3S$; phenyl-thienyl-acetoxime, $C_6H_5-C(NOH)-C_4H_3S$; aceto-thienone,[3] $C_4H_3S-CO-CH_3$; the hydroxylamine derivative of aceto-thienone, thienyl-methyl-acetoxime, $C_4H_3SCNOHCH_3$; the phenyl-hydrazine derivative of aceto-thienone, $C_4H_3SC\genfrac{}{}{0pt}{}{\diagup CH_3}{\leqslant N-NHC_6H_5}$, etc.

Baeyer's reaction, according to which condensation products are obtained by means of aldehydes and alcohols with benzene, takes place in an entirely analogous manner with thiophene;[4] thus, just as Baeyer obtained diphenyl-trichlor-ethane from chloral and benzene through the agency of sulphuric acid, so dithienyl-trichlor-ethane, $CCl_3-CH<\genfrac{}{}{0pt}{}{C_4H_3S}{C_4H_3S}$ is obtained from thiophene and chloral. Dithienyl-dichlor-ethylene, $CCl_2=C<\genfrac{}{}{0pt}{}{C_4H_3S}{C_4H_3S}$, phenyl-thienyl-methane, $CH_2<\genfrac{}{}{0pt}{}{C_6H_5}{C_4H_3S}$, and a number of other interesting bodies of this class, are known.

The Würtz-Fittig synthesis, by means of which higher members of the benzene series are produced, applied to thiophene[5] in exactly the same general manner as to benzene, yields homologues of thiophene.

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[1] O. Stadler, Berichte der deutschen chemischen Gesellschaft **18**, 1490.
[2] A. Comey, *ibid.* **17**, 790. [3] A. Peter, *ibid.* **17**, 2643. [4] A. Peter, *ibid.* **17**, 1341.
[5] Meyer and Kreis, *ibid.* **17**, 1558.

Mono-iodo-thiophene was used in these syntheses in preference to the corresponding bromine compound because of its more ready preparation; thus ethyl-thiophene was prepared according to the following equation:

$$C_4H_3IS + C_2H_5Br + Na_2 = NaBr + NaI + C_4H_3SC_2H_5.$$

In this way the following homologues have been prepared: Methyl-thiophene (thiotolene), $C_4H_3S - CH_3$; ethyl-thiophene, $C_4H_3S - C_2H_5$; normal propyl-thiophene, $C_4H_3S - C_3H_7$; normal butyl-thiophene, $C_4H_3S - C_4H_9$. The boiling-points of these bodies are almost identical with those of the corresponding benzene homologues.

The formation of diphenyl, $C_6H_5 - C_6H_5$, by conducting benzene through a tube heated to bright redness, finds its perfect analogy in the production of dithienyl,[1] $C_4H_3S - C_4H_3S$, by passing pure thiophene through a tube heated only to dull redness; a higher temperature than this causes thiophene to break up with formation of sulphuretted hydrogen and carbon.

The transformation of thiophene-sulphonic[2] acid, $C_4H_3S - SO_3H$, into the carbonic acid according to the method of Merz (by distillation of the potassium salt with potassium cyanide) takes place readily. By this reaction thiophene-nitrile, $C_4H_3S - CN$, is obtained, but the yield of this body is very decidedly less than that of benzene-nitrile in the analogous transformation of benzene-sulphonic acid. The conversion of the nitrile into the carbonic acid is effected in the usual manner, yielding the mono-carbonic acid (thiophenic acid), $C_4H_3SCO_2H$, the similarity of which to benzoic acid is simply astonishing.

The Würtz synthesis of benzoic acid from a halogen substitution product of benzene and the ethyl ester of chlor-carbonic acid, readily yields a thiophenic acid[3] according to the following equation:

$$C_4H_3SI + ClCOOC_2H_5 + 2Na = NaCl + NaI + C_4H_3SCO_2C_2H_5.$$

Structure of Thiophene.

The question, "What is the probable structure of thiophene?" is naturally at present one of the greatest interest. It has already been stated that Meyer proposed, almost at the beginning of the investigations in this field, a scheme which was based chiefly upon the marked resemblance which exists between thiophene, with the few derivatives at that time studied, and the benzene series. This structure, although of course suggested by and in accordance with the comparatively few facts at hand, was considered by its author as worthy of discussion, and valuable as a working hypothesis. The establishment of the structure of thiophene is certainly a task no more readily to be accomplished than the proof of the constitution of benzene, which, even after years of investigation, can hardly be regarded as furnished.

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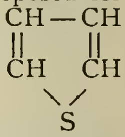
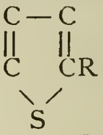
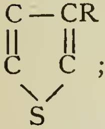
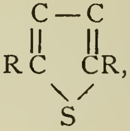
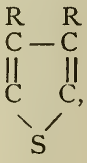
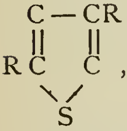
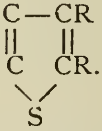
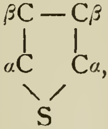
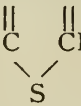
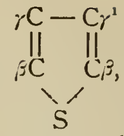
[1] R. Nahnsen, Berichte der deutschen chemischen Gesellschaft **17**, 789.

[2] Meyer and Kreis, *ibid.* **16**, 2172.

[3] R. Nahnsen, *ibid.* **17**, 2192.

In considering the probability of the structure[1] proposed for thiophene—*i. e.*, as represented in the following scheme,  questions in regard to the following points at once present themselves: the number of isomeric substitution products; formation o addition products; the position of the sulphur atom; the conduct of thiophene when oxidised, and the product thus formed; and, finally, the production of thiophene synthetically from substances of known composition. A not inconsiderable amount of valuable evidence upon a number of these points has already been accumulated, and although a few cases of what seems to be physical rather than chemical isomerism remain to be perfectly explained, still the scheme is in accordance with the facts known at present.

An inspection of this scheme shows that two mono-substitution products are theoretically possible—namely,  and ; four di-substitution products,    , .

The carbon atoms in this scheme were originally designated thus: , but since it was afterwards found that a number of compounds designated *a* were *chemically*, but not *physically*, identical with the *β*-compounds, and that the latter are really to be represented thus: , the original lettering of the carbon atoms was changed to the following: , the letter *α* being retained to designate the physical isomers, and having therefore no place in the structural scheme.

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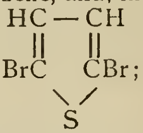
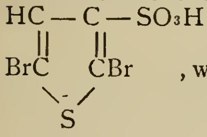
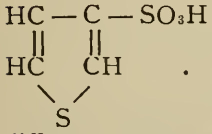
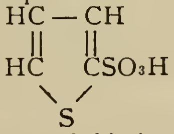
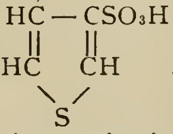
[1] Meyer, Berichte der deutschen chemischen Gesellschaft **18**, 526.

One of the first investigations[2] having for its object a study of the isomeric mono-substitution products was upon the sulphonic acids; one of these was prepared by direct treatment of thiophene with sulphuric acid; the other was obtained by introducing the sulpho group into dibrom-thiophene, and afterwards extracting the bromine by means of nascent hydrogen.[3] The position of the bromine atoms was not actually known, but it was assumed, on account of the perfect analogy which exists between thiophene and benzene in regard to substitution, that in thiophene as in benzene the two bromine atoms substitute the hydrogen atoms of those places which are separated by the greatest number of carbon atoms—*i. e.*, giving rise to para-dibrom-benzene, and, in the case of thiophene, to the following compound: ; this, by introduction of the sulpho group, would become:

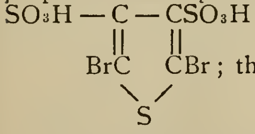


, which, by extraction of bromine, is converted into



. The two sulphonic acids produced in these different ways proved to be isomeric, and are then represented by the formulæ  and .

In the course of this investigation another body of interesting properties was produced—namely, dibrom-disulpho-thiophene,



; this gives a well-characterised anhydride:

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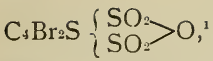
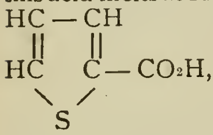
[1] Gattermann, Kaiser and Meyer, Ber. der deutsch. chem. Gesellschaft **18**, 3011.
[2] J. Langer, *ibid.* **17**, 1566. [3] Meyer, *loc. cit.*



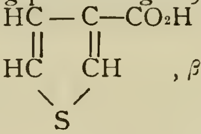
$C_4Br_2S\left\{\begin{matrix}SO_2\\SO_2\end{matrix}\right>O$,[1] which fact is an argument in favor of the immediate proximity to each other of the sulpho groups, and hence in favor of the above structural formula.

A consideration of the thiophenic (mono-carbonic) acids is of interest, because it presents what seems to be an example of physical[2] rather than chemical isomerism, as yet not explained. As already stated, a thiophenic acid was first formed by converting a salt of the sulphonic acid by Merz's synthesis into the carbonic acid; this acid melts at 118°; its structure was believed to be the following:



α-thiophenic acid.[3] Later, mono-iodo-thiophene was converted into a carbonic acid[4] by means of the Würtz synthesis; thus:

$$C_4H_3SI + ClCO_2C_2H_5 + 2Na = NaI + NaCl + C_4H_3SCO_2C_2H_5.$$

The acid thus obtained had different properties from the one from the sulphonic acid, its melting-point being 129°, and to it, therefore, was ascribed the structure,  , β-thiophenic acid.

A *third* thiophenic acid[5] was afterwards prepared by oxidising a methyl-thiophene, $C_4H_2S—CH_3$, which was the synthetical result of the action of phosphorus trisulphide upon sodium pyrotartrate; to this acid the name γ-thiophenic acid[6] was given. Not only was thus a third thiophenic acid prepared, but the synthetical methyl-thiophene[7] which produced it was also different from the two methyl-thiophenes already known; this was shown by the fact that the third methyl-thiophene yields a tribrom-methyl-thiophene different from the two already known. It is evident, then, that while Meyer's proposed structural scheme admits only two isomeric mono substitution products of thiophene, three methyl-thiophenes, three thiophenic acids, and also three tribrom-methyl-thiophenes, actually exist, while only two tribrom-methyl-thiophenes are possible according to the scheme.

These three apparent contradictions of Meyer's views in regard to the structure of thiophene have, however, been explained as follows:

The α- and β-thiophenic acids were converted into the dibrom-derivatives, $C_4HBr_2CO_2H$;[8] the α-derivative was obtained from the sulphonic acid resulting from direct treatment of thiophene with sulphuric acid; the β-derivative was obtained by oxidation of aceto-thienone, $C_4H_3S.CO.CH_3$, and treatment of the resulting carbonic acid with bromine. At first[1] the α-dibrom-thiophenic acid showed the melting-point 212°–213°, but, when re-obtained after conversion into the amide or the methyl ester, it showed a higher melting-point, 220°–221°, which is that of the β-acid; the amides and methyl esters were identical. It was further found[2] that dry distillation of the calcium salts of α- and β-thiophenic acid results in the formation of the same thienone, $C_4H_3S—CO—C_4H_3S$.

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[1] Berichte der deutschen chemischen Gesellschaft **17**, 1569.

[2] Meyer, *ibid.* **18**, 3008.

[3] Meyer and Kreis, *ibid.* **16**, 2172.

[4] Nahnsen, *ibid.* **17**, 2192.

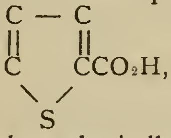
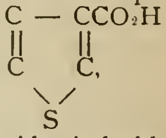
[5] Volhard and Erdmann, *ibid.* **18**, 454.

[6] F. Muhlert, *ibid.* **18**, 1770, 3003.

[7] Volhard and Erdmann, *loc. cit.*

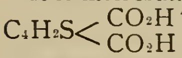
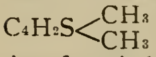
[8] A. Peter, *ibid.* **18**, 542.

It was therefore concluded[3] that, although α- and β-thiophenic acids are unquestionably different physically, since they furnish the same derivatives, they are chemically identical. (It will be remembered that mention has already been made of a similar kind of isomerism in connection with the dinitro-thiophenes, one of which is converted into the other by repeated distillation with water vapor.)

One of these thiophenic acids, β, is believed to have the composition , the other, γ, the composition  while the α, physically different from, but chemically identical with, β, is not of course specially designated in the structural scheme.

The apparent isomerism of three thiotolenes was accounted for by the discovery that thiotolene (methyl-thiophene) from coal tar is a mixture of the β- and γ-varieties, as proved by the fact that if a mixture of two parts of γ- to five parts of β-thiotolene be converted into tribrom-thiotolene, this latter compound is identical with that obtained from coal-tar thiotolene. This tribrom-thiotolene must then be a mixture of the β- and γ-products, but it has the peculiar property of not breaking up into its component bodies even by repeated crystallisations.

No facts, therefore, in view of these explanations, in regard to mono substitution products of thiophene, are at variance with Meyer's proposed structure.

It is interesting to note in regard to thiophene-dicarbonic acid,  $C_4H_2S<\begin{matrix}CO_2H\\CO_2H\end{matrix}$[4], that, although it has been prepared in five different ways, but one of the four theoretically possible isomers has as yet been obtained. The five different methods employed are as follows: From thiophene-disulphonic acid, from thioxene  $C_4H_2S<\begin{matrix}CH_3\\CH_3\end{matrix}$ by oxidation, from aceto-methyl-thienone by oxidation, from iodo-ethyl-thiophene, and from aceto-ethyl-thienone.

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[1] R. Bonz, Berichte der deutschen chemischen Gesellschaft **18**, 2308.

[2] L. Gattermann, *ibid.* **18**, 3014.

[3] Gattermann, Kaiser and Meyer, *loc. cit.*

[4] E. Schleicher, **18**, 3015, and also J. Rosenberg, *ibid.* **18**, 3031.

Syntheses of Thiophene and Homologues.

The syntheses of thiophene and its homologues thus far effected are of exceeding interest, not only in regard to the light thereby thrown upon the question of structure, but also because of the relation which they have shown to exist between thiophene, furfuran and pyrrol.

Ethyl sulphide $(C_2H_5)_2S$, when conducted through a red-hot tube, gives rise to a liquid which shows the indophenin reaction.[1]

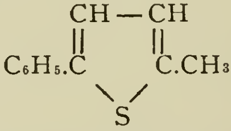
Ethylene, illuminating gas or ligroin vapors conducted over heated pyrites, give thiophene.

The color reactions obtained from the product of boiling crotonic acid with phosphorus sulphide indicated the production of thiophene. Normal butyric acid conducts itself similarly, but not so with isobutyric acid, whose composition, moreover, is not such as to indicate the possibility of yielding thiophene according to the proposed thiophene structure. Other syntheses of thiophene are of more value as indicating the structure of this substance.

C. Paal[2] has performed a number of very instructive syntheses in the furfuran, pyrrol and thiophene series, which are valuable as showing the high probability of a similar constitution in these bodies. The substance known as aceto-phenone-acetone, $C_6H_5CO - CH_2CH_2COCH_3$, when treated with substances capable of abstracting water, yields phenyl-methyl-furfuran, and the transformation is thus explained: In an intermediate stage of the transformation this substance passes into an unsaturated alcohol, and from this a molecule of water is given off as follows:

$$C_6H_5COCH_2CH_2COCH_3 = C_6H_5C.OH - CH.CH$$

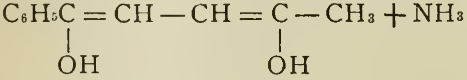
$$- C.OH - CH_3 =$$



$+ H_2O$.[3]

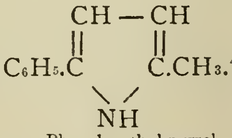
Phenyl-methyl-furfuran.

By the action of alcoholic ammonia upon the same body, aceto-phenone-acetone, phenyl-methyl-pyrrol is formed; this transformation is explained in a manner analogous to the above—namely, as follows: Aceto-phenone-acetone first goes through the intermediate stages and becomes an alcohol, which reacts with ammonia thus:



$$C_6H_5\underset{\displaystyle OH}{\underset{|}{C}} = CH - CH = \underset{\displaystyle OH}{\underset{|}{C}} - CH_3 + NH_3$$

$$= 2H_2O +$$



[4]

Phenyl-methyl-pyrrol.

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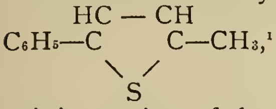
[1] Meyer, Berichte der deutschen chemischen Gesellschaft **18**, 217.

[2] *Ibid.* **16**, 2865; **17**, 2756; **18**, 367, 456, 688, 2251.

[3] *Ibid.* **17**, 2759.

[4] *Ibid.* **18**, 369.

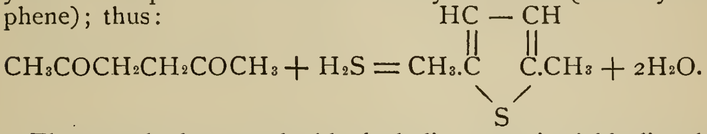
By heating aceto-phenone-acetone with phosphorus pentasulphide in a sealed tube to 120–130° for half an hour, 60 to 70 per cent. of the theoretical yield of phenyl-methyl-thiophene,



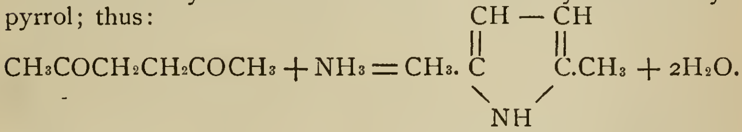
[1] is obtained; this body shows the characteristic reactions of the thiophene series with isatin and phenanthrene-quinone.

The preparation of these three analogous derivatives of furfuran, pyrrol and thiophene by appropriate treatment from one and the same body indicates that they have a similar constitution.

Similarly, also, the substance, acetonyl-acetone,[2] $CH_3COCH_2CH_2COCH_3$, when treated with phosphorus tri- or pentasulphide, yields a thiophene derivative—namely thioxene (dimethyl-thiophene); thus:

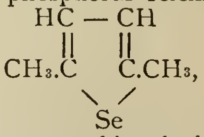


The same body treated with alcoholic ammonia yields dimethylpyrrol; thus:



The thioxene obtained as above showed great similarity to thioxene from coal tar, although it could not be affirmed with certainty that the two are identical.

Replacement[3] of phosphorus sulphide by phosphorus selenide gave the interesting substance seleneoxene,



in which selenium replaces the sulphur of thioxene; this selenium compound shows the isatin and phenanthrene-quinone color reactions.

Another synthesis was effected from mucic acid.[4] This substance by distillation, as is well known, yields a furfuran derivative, but if its ammonium salt be heated, it passes into pyrrol. These facts suggested the idea that by the action of hydrogen sulphide a thiophene derivative could be produced. After a number of attempts to realise this synthesis, success was attained by the action of barium sulphide upon mucic acid, producing a mono-carbonic acid of thiophene identical with that obtained by Nahnsen from iodo-thiophene. The reaction is thus explained:

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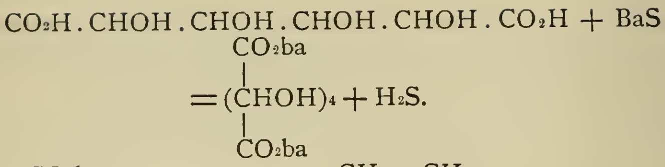
[1] Berichte der deutschen chemischen Gesellschaft **18**, 369.

[2] *Ibid.* **18**, 2251.

[3] *Ibid.* **18**, 2255.

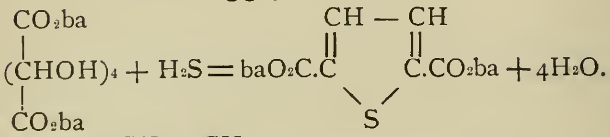
[4] Paal and Tafel, **18**, 456.

(I.)

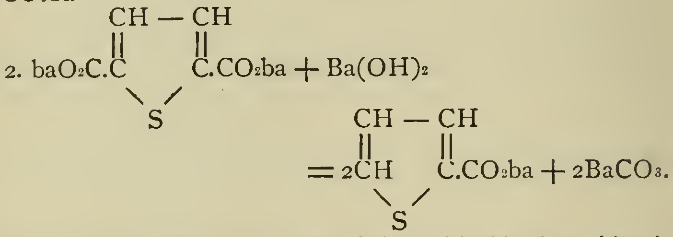


$$\mathrm{CO_2H.CHOH.CHOH.CHOH.CHOH.CO_2H + BaS} = \begin{array}{c}\mathrm{CO_2ba}\\ |\\ \mathrm{(CHOH)_4}\\ |\\ \mathrm{CO_2ba}\end{array} + \mathrm{H_2S}.$$

(II.)



(III.)



By distillation of the calcium salt of this acid, thiophene identical in every respect with thiophene from coal tar was obtained.

The interest and the importance of this synthesis are apparent, since, the constitution of mucic acid being known, the position of the carboxyl group in the thiophenic acid formed from it is at once determined as being that adjoining the sulphur atom, or which is now designated as the β-position.

Volhard and Erdmann[1] have also effected a synthesis of thiophene by heating a mixture of succinic anhydride and phosphorus pentasulphide. The thiophene produced is identical with that from coal tar.

Also, by treatment of sodium pyrotartrate with phosphorus trisulphide, the same authors have produced a thiotolene (methylthiophene) from which by oxidation was derived the γ-thiophenic acid already referred to.

The thiophene homologues, thiotolene,[2] $C_4H_3S{-}CH_3$, and thioxene,[3] $C_4H_2S{<}{\substack{CH_3\\CH_3}}$, have been obtained from commercial toluene and xylene, both of which were expected to contain these substances, since they show the Laubenheimer reaction.

As has already been shown, coal-tar thiotolene is a mixture of the β- and γ-isomers. Coal-tar thioxene has been proved by Paal's synthesis to be a β-dimethyl-thiophene.

Investigations having for their object the extraction of other higher homologues of thiophene from the analogous commercial benzene homologues are in progress. W. C. Day.

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[1] Berichte der deutschen chemischen Gesellschaft **18**, 454.

[2] Meyer and Kreis, *ibid.* **17**, 788, 1558; K. Egli, **18**, 544; Meyer, **18**, 1326.

[3] K. Schulze, **17**, 2852; J. Messinger, **18**, 563, 1636, 2300.

VALUATION OF COMMERCIAL PHOSPHATES.

An Agreement arrived at between the Chemists of the Experimental Stations and the Manure Manufacturers of South Germany, upon a New Basis for Establishing the Commercial Value of Superphosphate and Precipitated Phosphate.[1]

For the last twenty years the need has been felt for establishing a basis for determining the commercial value of phosphatic manures other than that dependent upon the amount of total and soluble phosphoric acid which they contain. Superphosphates made from such phosphates as Lahn phosphorite have, in consequence of their containing so-called "reverted" phosphate, a higher agricultural value than that indicated by the amount of phosphoric acid soluble in water which they contain; and since phosphatic manures consisting exclusively of precipitated phosphates insoluble in water have lately been brought in increasing quantities into the market, the need for some other basis for valuing manures has become more and more pressing.

R. Fresenius, in conjunction with Neubauer and Luck, found, as is well known, in neutral ammonium citrate, a salt which in solution of a suitable strength, and at a given temperature and time for extraction, proved serviceable enough for separating the precipitated phosphates from that portion of phosphorite superphosphate insoluble in water. This method, however, did not satisfy the requirements of the manure trade, inasmuch as the manurial value of this (reverted) phosphoric acid compared to that of phosphoric acid soluble in water was unknown. In order to solve this question, Petermann and Grandeau carried out some experiments, from the results of which they concluded that phosphoric acid soluble in citrate was of the same value as phosphoric acid soluble in water. This, however, was disputed in Germany, and the joint meeting of agriculturists and chemists held at Karlsruhe, in the year 1879, passed the following resolution:

"This meeting recognises the value of reverted phosphate for certain kinds of soil, and is in no way opposed to its determination, if required by the agriculturist or manufacturer, but considers that the experiments hitherto made do not furnish evidence sufficient to establish a valuation of reverted and precipitated phosphates."

Field experiments were now carried out, whilst at the same time a method was sought for to effect the determination of phosphoric acid soluble in the soil. Of the field experiments on the value of reverted and precipitated phosphates one has gradually become tired: they led to no issue, and it was impossible that they could do so. They have again been abandoned. Attempts to find a means, by merely laboratory operations, of determining phosphoric acid "soluble in the soil" have also proved fruitless, and it was indeed scarcely possible that they could succeed, since the very expression "phosphoric acid soluble in the soil" conveys no precise meaning, and, moreover, the means employed for this end could not themselves be held free from objection.

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[1] Translated and contributed to the Chemical News by H. H. B. Shepherd. From Chemiker Zeitung, 1886, **10**, 1, 2, 3.

Ammonium citrate, it has been urged, is an entirely unsuitable material for determining phosphoric acid "soluble in the soil," as it dissolves only insignificant quantities of phosphoric acid out of Peruvian guano, bone-meal and other similar manures which experience has shown contain much effective phosphoric acid. Free 1 per cent. citric acid, on the other hand, has been recommended as being far better, since it not only dissolves precipitated phosphate quite as well as does ammonium citrate, but it also takes up some 70 or 80 per cent. of the phosphoric acid contained in bone-meal and raw Peruvian guano, and shows besides that ground raw phosphorite contains about 4 per cent. of phosphoric acid soluble in the soil, which at any rate is correct, "for no agricultural chemist doubts that ground raw phosphorite used in large quantities *does* produce a certain amount of effect."

My own experiments have shown, however, that the manurial value of phosphoric acid soluble in 1 per cent. citric acid varies, according as it is presented to the plants in the form of precipitated phosphate of lime, washed-out high-class superphosphate, or finely ground phosphate. Supposing the manurial value of the phosphoric acid soluble in 1 per cent. citric acid to be represented by 100 in the case of precipitated phosphate of lime, its value in the case of washed-out high-class superphosphate would be represented by 160, and in the case of finely ground raw phosphorite by 2. Citric acid is therefore not a suitable means for dissolving out phosphoric acid from the different commercial phosphates in a manner that will compare with that effected by the soil and the roots of plants.

In addition, however, to ammonium citrate and free citric acid, potassium oxalate has been proposed as a menstruum, thus showing to what precision the whole question has shaped itself in the practice of the manure trade! Besides phosphoric acid soluble in water, the agriculturist can purchase now-a-days reverted phosphoric acid, phosphoric acid soluble in the soil, soluble in citrate or in citric acid, root-soluble, half-soluble, and precipitated-assimilable phosphoric acid; and he can have his analyses made by the methods of either Fresenius, Petermann, Halle (18th December, 1881), Tollens-Stutzer, or Liebig, or by the Anglo-Continental method; and if the agriculturist enquires what value is to be attached to these many-styled forms of phosphoric acid, he is told that this is not yet accurately known.

For some years I have been endeavoring to establish the groundwork necessary to throw some light upon this confused state of matters, and I proceeded upon the following lines: If the agriculturist be offered pure superphosphate of lime, it ought to be no difficult matter for him to obtain an opinion upon its value. If the manure merchant's price for phosphoric acid soluble in water averages about 58 pf. per kilo., the farmer knows that he will be right in paying 11 marks 60 pf. per 100 kilos. for a superphosphate containing 20 per cent. of phosphoric acid soluble in water. It is different, however, in the case of high-class and phosphorite superphosphates or precipitated phosphate. The buyer has then no idea in what relation the value of the precipitated phosphoric acid stands to soluble phosphoric acid of pure superphosphate of lime. If such manures are to be freely salable, one should be able to inform the agriculturist positively what percentage of phosphoric acid equal in manurial value to phosphoric acid soluble in water is contained therein. If this could be done, the buyer would be in a position to tell exactly how much he could afford to pay for the manure, and how it should compare as regards cost with pure superphosphate of lime. For the requirements of the manure trade, therefore, an analytical method is wanted which will give the phosphoric acid of phosphorite superphosphate, of high-class superphosphate, and of precipitated phosphate in their equivalents of phosphoric acid soluble in water, a method which will show how much per cent. of phosphoric acid of the manurial value of phosphoric acid soluble in water is present, or, in other words, the manurial value of the material expressed in terms of phosphoric acid soluble in water. Or, if we call such phosphoric acid simply "soluble" phosphoric acid, and agree that by this term we are to understand phosphoric acid of the same manurial value as phosphoric acid soluble in water, then the question presents itself as follows:

1. By means of manurial experiments to fix the relative manurial values of certain phosphatic manures expressed in terms of "soluble" phosphoric acid—*i. e.*, in terms of phosphoric acid of the same manurial value as phosphoric acid soluble in water.
2. To find an analytical method which shall furnish results agreeing exactly with the percentage of "soluble" phosphoric acid obtained by the manurial experiments.

This question has been my study during a long series of years. As regards the carrying out of my experiments, however, and the details which had to be taken into consideration, I must here confine myself to merely cursory references.

The manures which I used were the following:

1. Pure superphosphate of lime.
2. A commercial precipitated phosphate of lime, prepared by precipitation in a strongly acid solution, and termed dicalcium phosphate.
3. A commercial precipitated phosphate of lime, precipitated with excess of lime, and termed tricalcium phosphate.
4. A washed-out high-class superphosphate.
5. A washed-out phosphorite superphosphate.
6. Finely ground raw phosphorite.

I thought it unnecessary to include also the superphosphates 4 and 5 in the original unwashed-out condition, as, in the presence of so overwhelming an amount of phosphoric acid soluble in water, the effect of the precipitated phosphate contained in them would not have been sufficiently marked. The washing-out of the superphosphates was itself a matter for careful consideration, inasmuch as variations, both qualitative and quantitative, in the precipitated phosphoric acid, arise according as the wash-water at first poured upon the superphosphate is allowed to filter faster or slower through the mass. The quantity of the wash-water used and the length of time occupied by the washing have also their influence, and the variations thus caused would be sufficient to affect the results of the manurial experiments to such a degree as to render the carrying of them out in practical working inadmissible. In the examination of this question I now started with the following consideration: It is necessary in superphosphates to distinguish between—

1. The phosphoric acid which goes into solution on treating 20 grams of superphosphate with 1 litre of water for two hours; and,
2. The phosphoric acid which remains undissolved in the residue.

The manurial value of the phosphoric acid referred to under 2 must be obtained by means of manurial experiments, and a suitable material for such experiments can be prepared by digesting 20 grams of superphosphate in 1 litre of water, or 200 grams in 10 litres, for two hours, with frequent shaking, collecting the residue upon a filter, and, without further washing, allowing it to dry at the ordinary temperature of the air. In this way I produced the so-called washed-out superphosphates. I must further remark that I carried out the experiments in zinc vessels holding about 16 kilos. of earth, and that I experimented upon three kinds of soil—viz., sandy soil poor in lime, loamy soil containing lime, and Rhenish-Hessian soil rich in line. The moisture in the soil was kept as constant as possible, and at about the medium percentage (10 to 15). The crops upon which I experimented were barley, oats, peas and grass.

I have already frequently expressed myself concerning the peculiarities of the results obtained by my method, but I now briefly communicate the following:

1. The phosphoric acid found in bicalcium phosphate by the Fresenius method proved equal in value to 100 per cent. of phosphoric acid soluble in water.
2. The phosphoric acid found in the tricalcium phosphate by the Fresenius method proved equal in value to 75 per cent. of phosphoric acid soluble in water.
3. The phosphoric acid found in the washed-out high-class superphosphate and phosphorite superphosphate by the Fresenius method proved, on the average, equal in value to 70 per cent. of phosphoric acid soluble in water.

I must here remark that these data have reference to the action which the phosphates, applied in the spring at seed-time, exercised on the crops; the so-called "after-effects" of the phosphates are therefore left out of consideration. Arrangements for carrying out the experiments so as to show indubitably the after-effects of the manures have only been at my disposal since the beginning of the year 1885, and I have naturally not been able to bring the work in connection with them to a conclusion.

4. The results of the manurial experiments give the following percentages of "soluble" phosphoric acid—*i. e.*, of phosphoric acid equal in value to phosphoric acid soluble in water—contained in the manures used:

	"Soluble" phos. acid.
Bicalcium phosphate, ...	30.6 per cent.
Tricalcium "	16.4
Washed-out high-class superphosphate, . .	17.9
Washed-out phosphorite superphosphate, .	3.0
Finely ground raw phosphorite, . . .	0.1

Having obtained these results, the first part of my task was accomplished. In five different phosphatic manures the percentages of "soluble" phosphoric acid was obtained, and it still remained to find a menstruum which under the same circumstances would dissolve phosphoric acid out of each manure in the above proportions—that is to say, 30.6 per cent. out of bicalcium phosphate, 16.4 per cent. out of tricalcium phosphate, and 17.9 per cent. out of washed-out high-class superphosphate.

After many experiments with all possible organic acids I arrived at the same conclusion as Tollens and Stutzer—viz., that of all organic acids, citric alone can be considered admissible; but even this acid, or at any rate the exclusive use of it, proved unsuitable, since its action upon phosphate of iron and alumina is too weak in comparison with its action upon phosphate of lime. I therefore made experiments with its ammonium salts, and came to the same opinion as Fresenius—viz., that of all salts of citric acid, only the ammonium citrate can be considered available. It followed from this that in a suitable mixture of neutral ammonium citrate and free citric acid the properties of both would combine to form a solvent available for the various phosphates. A few preliminary experiments confirmed this supposition.

Now that the preliminaries of the required method had been decided upon, I determined to take into consideration the details of the process and all the practical requirements necessary for a method intended to further the object in view.

I essentially kept in mind the following considerations:

1. The method must allow of superphosphate being treated directly—*i. e.*, without having first to remove the phosphoric acid soluble in water.

2. In order that there may be no difficulty in obtaining a representative sample, sufficient of the material under examination must be taken for extraction (at least 5 grams per ½ litre).

3. The length of time to be decided upon for the extraction must be such that in the event of 30 or 40 superphosphates being in hand at once they can be dealt with without inconvenience. The longer the time agreed upon for extraction, the less likely can any deviations from such time affect the results; and provided it be observed within an hour one way or the other, I recommend as most convenient that the period for extraction be from one day to the next.

4. Also the prescribed degree of temperature must be such as to render its maintenance easily controlled, so that deviations may not lead to differences. The so-called temperature of the room, 13° to 18° C., is most to be recommended.

5. The method must admit of the substance being rubbed fine, for in no other way can uniformity in the results be obtained.

6. A sufficient quantity of the menstruum must be available for rubbing up the substance. 100 cc. of citrate solution are not enough for conveniently dealing with 5 grams of substance.

7. The determination of the phosphoric acid must be made in the extract and not indirectly in the residue, and the phosphoric acid must be precipitated by molybdenum, so that the results turn out exact and reliable.

Having regard to these seven essentials, I arrived, after many experiments, at the following method: 5 grams of superphosphate or precipitated phosphate are rubbed up with some dilute citrate solution, poured into a half-litre flask, made up to the mark with dilute citrate solution, allowed to stand about 18 hours at the temperature of the room (13° to 18° C.), with frequent shaking, and then filtered.

50 cc. of the filtrate are then treated with molybdenum solution, so that 1 cc. shall be present for every milligram of phosphoric acid, and to this mixture as much concentrated ammonium nitrate solution is added as would amount to a fourth of the mixture. After standing for about twenty minutes in the water-bath it is allowed to cool and is then filtered; the precipitate is washed on to the filter with a dilute solution of ammonium nitrate, a hole made in the filter, and the precipitate washed back into the beaker with dilute ammonia (2½ per cent.); the filter is well washed, and to the ammoniacal solution 20 cc. of magnesia mixture are added drop by drop with constant stirring. After standing for one hour the precipitate is filtered off, washed with dilute ammonia (2 per cent.), dried and ignited.

Preparation of the Necessary Solutions.

1. Concentrated citrate solution. 150 grams of citric acid are placed in a litre flask, dissolved in water, and neutralised with ammonia. To the neutralised solution 10 grams of citric acid are added, and the solution made up to the mark with water.

2. Dilute citrate solution. 1 volume of concentrated citrate solution is mixed with 4 volumes of water.

3. Concentrated ammonium nitrate solution. 750 grams of ammonium nitrate are dissolved in water and the solution diluted to a litre.

4. Dilute ammonium nitrate solution. 100 grams of ammonium nitrate are dissolved in water and the solution diluted to a litre.

5. Molybdenum solution. 150 grams of ammonium molybdate are dissolved in water, the solution diluted to a litre, and mixed with a litre of nitric acid of sp. gr. 1.2.

6. Magnesia mixture. 110 grams of pure crystallised magnesium chloride and 140 grams of ammonium chloride are dissolved in 1300 cc. of water and 700 cc. of ammonia (8 per cent.).

I now give the results I obtained by this method in comparison with those calculated from the mean results of the manurial experiments.

"*Soluble*" *Phosphoric Acid.*

	Calculated from the results of the manurial experiments. Per cent.	Obtained by analysis. Per cent.
Bicalcium phosphate, ...	30.6	29.3
Tricalcium "	18.0	19.1
Washed-out high-class superphosphate, .	17.9	16.9
" phosphorite " .	3.0	3.3
Finely ground phosphorite, . . .	0.1	0.6

These results agree satisfactorily, and it may be reasonably accepted that my method gives figures which show sufficiently near the truth the agricultural value of phosphorite superphosphate, high-class superphosphate, and precipitated phosphate in terms of phosphoric acid soluble in water.

It is now self-evident that the method could be further developed, and had not external pressure been brought to bear upon me, I would have hesitated before proposing to introduce it at once into the practice of the manure trade. Requests to make determinations of phosphoric acid soluble in citrate in the above-named manure materials have, however, been so frequent of late at the experimental stations at Bonn, Darmstadt, Speier and Wiesbaden that the immediate introduction of the method appeared very necessary.

At a meeting of those manure manufacturers of South Germany chiefly interested, held at Mayence on November 30th, 1885, and called at the instance of the experimental stations of Bonn, Darmstadt, Marburg, Speier and Wiesbaden, I found myself called upon to report upon the work I had carried out, and to apply to them to test my process as to what extent in the various laboratories concordant results could be obtained. In consequence of this request the meeting appointed representatives of four experimental stations and four manure works as a commission, which carefully drew average samples of 8 different phosphatic manures and distributed them amongst 12 laboratories, and at a further meeting held at Mayence, on December 19th, reported upon the results obtained.

From the returns furnished by 11 of the laboratories it was ascertained that the variations between the separate results and the mean averaged as follows:

		Per cent. "soluble" phosphoric acid.
With high-class superphosphate, . .	I	= ±0.27
" " " . .	II	= 0.38
With phosphorite " . .	III	= 0.30
" " " . .	IV	= 0.32
	Mean	= ±0.32

Against this the variations in the determinations of the phosphoric acid soluble in water made by the same chemists amounted to—

		Per cent. phosphoric acid soluble in water.
With high-class superphosphate, . .	I	= ±0.39
" " " . .	II	= 0.36
With phosphorite " . .	III	= 0.13
" " " . .	IV	= 0.18
	Mean	= ±0.26

From this we see that the mean differences in the determinations of the "soluble" phosphoric acid exceed those of the phosphoric acid soluble in water by only 0.6 per cent. The representatives of the manure manufacturers and those of the experimental stations of Bonn, Darmstadt, Speier and Wiesbaden have therefore agreed unanimously to accept this method for the analysis of all superphosphates from January, 1886, and in consequence thereof, to advertise in their price lists a guaranteed percentage of "soluble" phosphoric acid in the different superphosphates.

In the case of Thomas precipitated phosphate the results obtained were not sufficiently concordant, and the commission was requested to look closer into the matter and to report again in due course.

It is now to be hoped that the convention which met at Mayence, as well as all other manure manufacturers and agricultural chemists, will co-operate in this movement, in order that through the instrumentality of this agreement this most desirable reform in the trade in precipitated or "reverted" phosphates may be carried out in the interests of buyers and sellers alike.

PAUL WAGNER.

STUDIES FROM THE LABORATORY OF PHYSIOLOGICAL CHEMISTRY, SHEFFIELD SCIENTIFIC SCHOOL OF YALE COLLEGE, 1884–85. Edited by R. H. CHITTENDEN, Ph. D. New Haven: Tuttle, Morehouse & Taylor. 1885.

The appearance of this volume of 200 pages, in addition to the numerous articles from this laboratory that have been published in the journals, is a pleasant surprise to those interested in physiological chemistry. The "Studies" consist of eleven papers contributed by Prof. Chittenden and his co-workers. The first seven of these are devoted to a record of investigations on the soluble ferments, with special reference to the action of various agents on these bodies. These experiments are of unusual interest at the present time, when so much attention is being given to similar observations on the organised ferments. The similarity that is shown to exist between the action of most agents on the two classes of ferments suggests the question as to how far the antiseptic value of an agent is dependent on its action on the soluble ferments secreted by the organism. It is to be hoped that work of this character will place our knowledge of antiseptics on something more than the present empirical basis. The disputed point concerning the amount of acid necessary to prevent the action of diastase is taken up by the authors, and they show that it depends simply upon the amount of proteid matter in the solution, the acid combining with this to form acid-proteids, which act very differently from free acid.

A short paper on "Absorption of Arsenic by the Brain" gives two new cases in support of the editor's view, "that the amount of arsenic present in the brain, in cases of arsenical poisoning, is an index to the form in which the poison was taken."[1]

Two papers on the "Influence of Potassium and Ammonium Bromides," and of "Cinchonidine Sulphate on Metabolism," are of considerable physiological interest.

The concluding paper is devoted to a review of the work of Seegen and others on the "Post-mortem Formation of Sugar in the Liver in the Presence of Peptones," and contains also a large number of additional experiments on this subject. The conclusions reached by the authors appear to be decisive, from the fact that they have overcome the principal difficulty of former investigators —viz.: that of making accurate determinations of the various hydrocarbons in the presence of albuminoid matter.

The volume owes its interest both to the importance of the subjects investigated, and to the large amount of careful work from which the results have been obtained. The introduction of accurate chemical analyses into physiological research seldom fails to be of use to both sciences. J. R. D.

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[1] This Journal **5**, 8.

NOTES.

Editor AMERICAN CHEMICAL JOURNAL.

SIR :—As a large number of persons employ Laurent's polariscope for the estimation of sugar, I desire to call their attention, through your Journal, to a peculiarity in the method of graduation which has the effect of making all the results obtained with the instrument too low. I had prepared a paper explaining the matter at length, as it had gradually made itself known to me, but to-day see in the *Bulletin de l'Association des Chemistes* **3**, 255–259, an article by D. Sidersky correcting the same error. I therefore merely wish to bring the main points before your readers, referring them to the original paper of Sidersky for greater details.

The Laurent instrument is graduated with a plate of quartz and not with a definite solution of pure sugar. The plate of quartz is exactly one millimeter thick, and it is accepted by Laurent from the researches of Girard and De Luynes that this has an angular rotation of 24°40′ corresponding to a sugar solution containing 16.19 grams per 100 cc. Recent researches of Tollens and Schmitz have independently shown that the $[a]_D$ for a concentration of about ten per cent. is 66.5°, and this is without doubt the most reliable figure we have to-day to go by. Comparing Laurent's graduation with this, we see that the normal weight for his instruments is somewhat at fault. From his data he makes 100° of the sugar scale correspond to 24°40′ of the angular. Combining these figures with the specific rotatory power given by Tollens for solutions of about normal strength in the well-known formula,

$$[a]_D = \frac{100a}{lC},$$

we get from our data, where the usual 200 mm. tube is used,

$$66.5^\circ = \frac{100 \times 24.6666}{200 \times C} \quad \text{or } C = \frac{246 \times 6.66}{133.0}.$$

The construction or normal weight calculated from this equation is 16.29, or a tenth of a gram more than Laurent gives as the correct one for his instrument; but it is undoubtedly the correct one to use, as has been proved by Sidersky, and by experiments in the Laboratory of the Department of Agriculture.

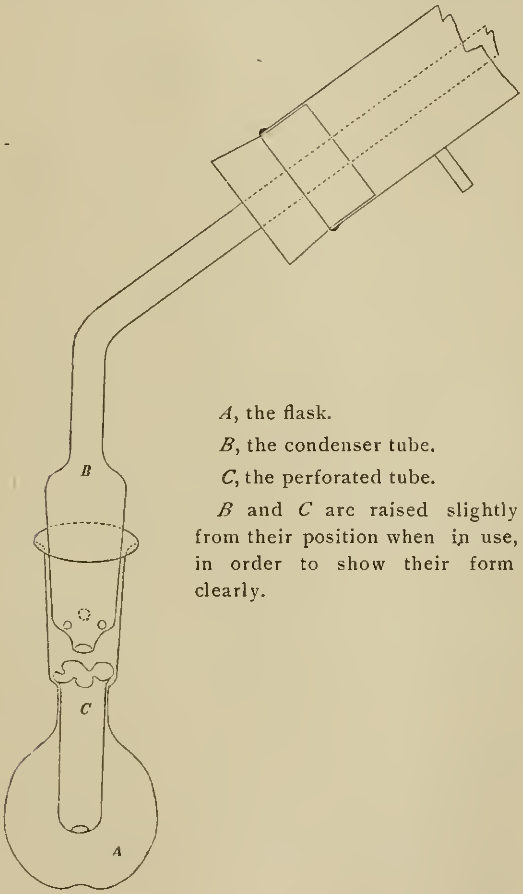
Trusting that this note may prove of interest to some of your readers, and save them from some annoyingly low results in polarising high-grade refined sugars, I am

Very truly yours,

CLIFFORD RICHARDSON.

On a New Apparatus for the Continuous Extraction of Solids by a Volatile Solvent.[1]

The authors have devised a new form of extraction apparatus which is so satisfactory to them that they think that a brief description of it may be of interest to other chemists. It consists of three parts: the flask *A*, the condenser *B*, and the perforated tube *C*. The flask is 14–15 cm. in height, and weighs about 45 grams. The upper part of the neck is ground to fit the condenser, and is 3 cm. in diameter. The lower part of the neck contracts suddenly to 2.5 cm. in diameter, thus presenting an annular projection within which supports the perforated tube. The tube of



A, the flask.

B, the condenser tube.

C, the perforated tube.

B and *C* are raised slightly from their position when in use, in order to show their form clearly.

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[1] This apparatus was described before the Kansas Academy of Science, Nov. 11, 1885.

the condenser is about 75 cm. long, and has an internal diameter of 8 mm. Near the lower end it is bent at an angle of 60°, and passes upward through a copper tube 3–4 cm. in diameter, supplied with cold water when in use. At its lower end the condenser tube expands into a stopper for the flask, and at its extremity is brought nearly to a point, to direct the dropping of the condensed solvent. Three additional openings are made in the stopper-expansion to allow the vapor free passage upward. The perforated tube is similar to a short, wide test tube, with a perforation in the bottom. The lip of the tube is notched to give openings for the passage of the vapor. The body of the tube must pass readily through the contraction in the neck of the flask, and at the same time the lip must rest securely on the inner projection. The lower end of the tube may reach within 1.5–2 cm. of the bottom of the flask.

The mode of using the apparatus is almost obvious. The substance to be treated is confined in the perforated tube between two layers of asbestus, a sufficient amount of the volatile solvent is placed in the previously weighed flask, and the parts are put in place and suitably supported. Upon heating the solvent by means of a water-bath, the vapor is evolved with any rapidity desired, and passes into the condenser. The condensed solvent flows uninterruptedly down the same tube, drops into the perforated tube, filters through the substance to be extracted, and passes back into the flask. After the operation has been continued as long as is desired the perforated tube is removed, the apparatus inclined so as to carry the condensation out instead of back, and the solvent distilled off. The solvent may thus be recovered, which is a matter of no small importance where ether is used and many determinations are to be made. The flask, with the substance extracted, is then carefully dried and weighed.

The chief advantages of this extractor are its simplicity, and consequent convenience of handling, and its freedom from corks which come in contact with the solvent. It avoids the slender tubes and multiplicity of connections so common in extractors, and at the same time can be manufactured at a very moderate cost. Every chemist knows the difficulty and inconvenience of completely removing the soluble substances from corks, but if it is desired the flask can be made without having the neck ground, and it can be connected by a cork to an inverted Liebig's condenser. In this form the extractor is still cheaper, and, even with the one cork, is more desirable than any other form that has come under our notice.

This apparatus was designed for quantitative work, but, with some modifications, might be adapted to pharmaceutical operations. The flask would have to be made deeper and the neck much wider, so as to admit a large perforated tube. The flask could be connected with the condenser by means of a broad ring of glass, ground on its outer edge to fit the neck of the flask and within to fit the condenser tube. In that way an apparatus could be constructed of considerable capacity, and, we think, at less cost than those now in use.

G. H. FAILYER AND J. T. WILLARD.

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The Action of Nitric Acid on Mercuric Sulphide.

Probably many chemists have had their attention called to the difficulty in the qualitative determination of mercury mentioned in Prof. Torrey's note in the JOURNAL for December, '85. Following Fresenius, most manuals of qualitative analysis state that the mercury is found as a black, insoluble residue after the mixed sulphides are treated with nitric acid. The manual of Dr. F. P. Venable (Univ. of N. C.) is the only one in my knowledge which mentions that "the residue may be HgS (black), $(HgS)_2\,Hg(NO_3)_2$ (*white*)," etc.

Most authorities state that HgS is unaffected by dilute nitric acid. Watts says (Vol. III, p. 913), "It (HgS) withstands the action of most solvents, but is decomposed with separation of sulphur by very strong nitric acid; dilute nitric acid *has scarcely any action upon it*" (italics mine); which in the first supplement is modified to "mercuric sulphide, which under ordinary circumstances is insoluble in nitric acid, is likewise converted, by prolonged heating with that acid, into the white compound $Hg(NO_3)_2\,2HgS$" (Vol. VI, p. 818).

In my own experience I have been unable to effect any change in mercuric sulphide by boiling with pure nitric acid (sp. gr. 1.42), but on the addition of a single drop of dilute hydrochloric acid (1 : 3) to the boiling nitric acid, the sulphide was immediately converted into a yellowish-white compound, presumably the $Hg(NO_3)_2\,2HgS$. On the addition of a very small further quantity (say ten drops) of the dilute hydrochloric acid, this white compound dissolved easily and completely. The sulphide was also easily acted on by boiling dilute nitric acid when a very small quantity of hydrochloric acid was present, and dissolved to some extent.

Now, since most nitric acid, except reliable c. p. acid, contains traces of hydrochloric acid, it will be easily understood how these differences of opinion have originated, and that the mercury must not be overlooked in the white residue, after treating the mixed sulphides with dilute nitric acid.

I have often known traces of mercuric sulphide to be thus dissolved, and, since the precipitate of mercuric nitrate with ammonia, like that of cadmium and copper, is easily soluble in excess of ammonia, and in this solution is not precipitated by potassium cyanide, to be precipitated by hydrogen sulphide in the test for cadmium.

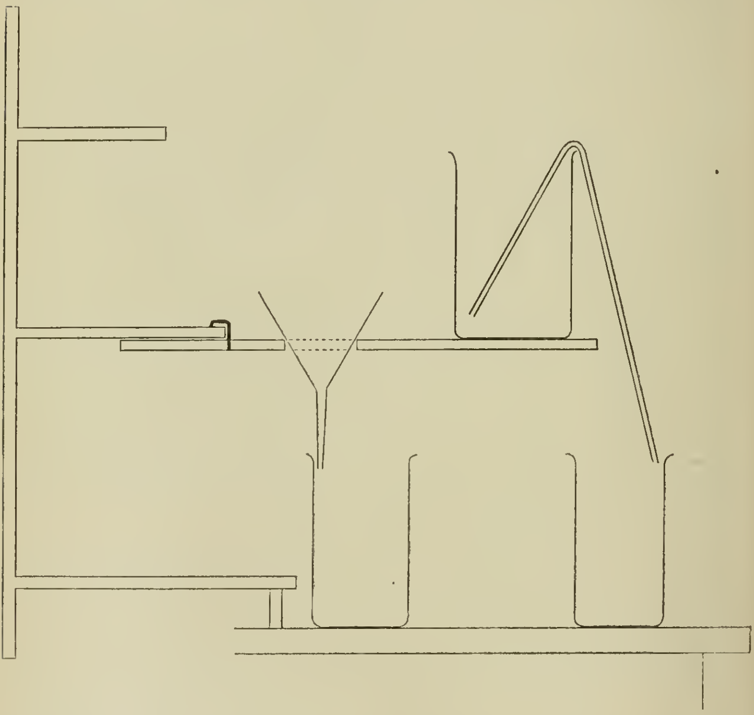
The moral of this is to use only a nitric acid which is known to be pure for the solution of the mixed sulphides.

JAS. LEWIS HOWE.

LABORATORY OF CENTRAL UNIVERSITY, RICHMOND, KY., *January*, 1886.

A New Funnel Support.

The following simple device will often be found of use on the working desk in the laboratory, where space must be economised. It consists of a piece of dressed inch plank about 20 by 8 inches; at a distance of 5 or 6 inches from one end two stout wrought-iron hooks are driven and clinched. The working desk must be provided with firmly fixed shelves, such as are usually employed for reagents. The end of the plank is pushed under a shelf and is held in place by the hooks, which catch upon the edge of the shelf. The portion of the plank projecting over the desk may then be employed as a support for funnels, percolators, etc. The figure presents in part a cross-section of a desk with the support in use.



A support of this description, in which six or more holes of different sizes are cut, will often replace several filter stands, tripods, etc., which require so much more space for their accommodation, both when they are in use and when out of use.

F. P. DUNNINGTON.

UNIVERSITY OF VIRGINIA, *January*, 1886.

VOL. VIII. [MAY, 1886.] NO. 2.

AMERICAN

CHEMICAL JOURNAL.

ON THE REICH METHOD OF DETERMINING ARSENIC.

BY LEROY W. MCCAY.

In the year 1864 there was introduced by Reich into the assay laboratory of the Royal Smelting Works at Freiberg, Saxony, a method for determining arsenic in ores and metallurgical products, based upon the fact that arseniate of silver is insoluble in water. The method, subsequently modified by Richter, has been in exclusive use at the laboratory of the Works ever since the period of its introduction. This fact speaks for its success.

The following short description of the process is taken from Post's *Chemische Technische Analyse:*

About 0.5 gram of the finely pulverised substance is digested in a porcelain crucible, covered with a watch-glass, with concentrated nitric acid and under the influence of heat, until the residue assumes a lighter color and the sulphur which separates out has become of a pure yellow hue. After decomposition the glass is rinsed with a few drops of water, and the uncovered crucible heated upon the sand-bath in order to get rid of excess of acid. A complete evaporation is to be avoided. Four grams of sodium carbonate are now added, the mass is completely dried upon the sand-bath, four grams of potassium nitrate are introduced into the crucible, and the same is heated until its contents flow quietly. The melted mass is permitted to remain in this state for ten minutes. After the crucible is cool it is brought into a dish, the fused mass is extracted with hot water, and the resulting solution filtered. The alkaline liquid which contains the arsenic as arseniate of sodium is acidified with a small quantity of nitric acid, placed for two hours upon a hot sand-bath, in order to get rid of the carbon dioxide, mixed with a sufficient amount of silver solution, and then carefully neutralised with dilute ammonia. Reddish-brown arseniate of silver is precipitated. The precipitate is filtered off, washed, well dried, shaken from the filter upon glazed paper, and the folded filter paper brought into a scorifier and ashed in a glowing muffle. When the scorifier is cold the precipitate is added to the remains of the filter, the scorifier charged with ten assay tons of lead, and the combined silver estimated in the ordinary way. From the silver found the arsenic present is calculated: $100\ Ag = 23.15\ As$.

In 1883 I published an article upon a modification of this method, which will be found in the *Chemical News*, Vol. 48, No. 1232, p. 7. A few weeks before the appearance of my article I noticed in *Science*, Vol. 1, No. 15, a short account of Reich's method by Mr. Pearce, of the Colorado Smelting Works at Argo, Col. A detailed description by Mr. Frost of this modification of the process was published in the *Engineering and Mining Journal*, Vol. 35, p. 256, and subsequently copied into the *Chemical News*, Vol. 48, No. 1239, p. 85.

My modification of the Reich method differs from that of Mr. Pearce in that it is essentially a method of *rest*. In fact, while working up the process, I followed very closely the mode of procedure recommended by Drs. Kratschmer and Sztancovánszky in their volumetric method for determining phosphorus.[1] Mr. Pearce's modification consists in dissolving the arseniate of silver in nitric acid and titrating the silver with thiocyanate of ammonium according to Volhard.

During the last two years I have had ample opportunity for thoroughly testing this silver method for estimating arsenic. In conjunction with several of my pupils, among whom I am especially indebted to Mr. J. W. Phillips, the process has been subjected to an exhaustive examination, and since numerous improvements have grown out of our work, it seemed desirable to again write a description of the entire matter, directing attention to many little details which were omitted in the first paper, to the most accurate practical way of conducting the analysis of ores and metallurgical products, and, above all things, to a gravimetric modification which renders it possible to get results more accurate perhaps than those obtained by Mr. Pearce's volumetric process.

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[1] Zeits. für analy. Chem. **21**, 523.

Nitrate of silver throws down from solutions of di- and tri-metallic alkali arseniates a highly characteristic reddish-brown precipitate of arseniate of silver which is readily soluble in ammonia and acids, but insoluble in water. If the solution contained a tri-metallic arseniate the fluid in which the precipitate is suspended exhibits a neutral reaction, whilst the reaction is acid if the solution contained a di-metallic arseniate. The acid reaction in this latter case arises from the fact that the nitric radical receives, for the three atoms of silver which it surrenders to the arsenic acid, only two atoms of alkali metal and one atom of hydrogen:

$$Na_2HAsO_4 + 3AgNO_3 = Ag_3AsO_4 + 2NaNO_3 + HNO_3.$$

By a suitable neutralisation of this molecule of free acid the filtrate from the precipitate can be shown to contain no arsenic.

Since this subject of neutralisation is of immense importance, and since there seems to exist in the minds of some chemists a doubt respecting the possibility of obtaining a neutralisation so complete as to occasion a separation of all the arsenic and yet avoid the precipitation of oxide of silver, in the minds of others a suspicion that the arseniate of silver is not absolutely insoluble in the nitrate of ammonium formed, I think it were well to begin by discussing the relations which hold between arseniate of silver and the hydrate and nitrate of ammonium. I can accomplish my purpose best by directing attention to the following experiments:

Experiment 1.—1 cc. of an ordinary solution of nitrate of silver was brought into a small beaker, diluted to 25 cc., and heated to boiling. It was then rendered faintly but distinctly alkaline with ammonia. No precipitate settled as long as the liquid was hot. Upon cooling a faint opalescence made its appearance, and, after standing over-night, the liquid had deposited a very small precipitate of oxide of silver—a quantity, however, too minute to filter and examine.

Experiment 2.—2 cc. of the solution of nitrate of silver were brought into a beaker, diluted to 50 cc., and a few small crystals of ammonium nitrate added. The liquid was then heated to boiling, removed from the flame, and rendered faintly but distinctly alkaline with ammonia. No precipitate of oxide of silver appeared; none had made its appearance at the end of an hour, after the expiration of which time the liquid had cooled to the temperature of the laboratory; nor could I, even after allowing the solution to stand forty-eight hours, detect the smallest precipitate of oxide of silver. (1) 10 cc. of this solution gave, with one drop of a solution of arsenic acid = 0.00025 gram arsenic, an immediate and decided precipitate of arseniate of silver. (2) 10 cc. of the solution gave, with one drop of a solution of arsenic acid = 0.0001 gram arsenic, an immediate and distinct precipitate of arseniate of silver. (3) 10 cc. of the solution gave, with one drop of a solution of arsenic acid = 0 00005 gram arsenic, an extremely faint but, nevertheless, instantaneous cloudiness, which, upon permitting the liquid to stand, separated as a tiny red precipitate.

Again, the following experiments:

Experiment 1.—5 cc. of a solution containing about 14.45 grams H_2KAsO_4 per litre were brought into a small beaker, 100 cc. water added, and the contents of the beaker heated to boiling. A sufficient quantity of nitrate of silver to combine with the arsenic was then added, the beaker was removed from the flame, and its contents were rendered faintly but distinctly alkaline with dilute ammonia. After stirring briskly and prolongedly, so as to coagulate the arseniate of silver and cause it to settle rapidly and completely, the beaker was put aside until its contents were cool. The liquid was then filtered and the precipitate washed by decantation until the washings gave no reaction for silver. The precipitate in the beaker was covered with 100 cc. water and allowed to stand twelve hours. 25 cc. were next filtered into a Nessler cylinder and tested for silver with hydrochloric acid, but with a negative result. The original filtrate from the arseniate of silver was treated with hydrochloric acid, the chloride of silver filtered off, and the filtrate from the same saturated with sulphuretted hydrogen. In three days no sulphide of arsenic had separated. The flask containing the filtrate was kept in the dark and well corked.

Experiment 2.—The above experiment was repeated with 10 cc. H_2KAsO_4 solution, but the results were identical with those obtained with 5 cc.

Experiment 3.—The experiment was tried a third time, and with 20 cc. H_2KAsO_4 solution. The results were the same as in both previous cases.

These five experiments go to show:

a. That a solution of nitrate of silver containing small quantities of nitrate of ammonium can be made faintly but distinctly alkaline and yet no oxide of silver will separate out.

b. That when a solution of an alkali arseniate, after the addition of nitrate of silver, has been rendered neutral or faintly alkaline to delicate litmus paper, the precipitation of the arsenic as arseniate of silver is complete.

c. That arseniate of silver is to all intents and purposes insoluble in water containing *small* quantities of nitrate of ammonium.

Why, when the reaction of the liquid in which the arseniate of silver is suspended proves faintly but distinctly alkaline, there should be no perceptible action of the ammonia on the reddish-brown precipitate I am unable to say with certainty. I think, however, that the explanation is this: There is really *no* free ammonia present. The alkaline reaction of the liquid is due to the oxide of silver formed by the action of the ammonia on the excess of nitrate of silver and kept in solution by the small amount of ammonium nitrate present.[1] A solution of oxide of silver in ammonium nitrate gives a strong alkaline reaction.

The Reich method for estimating arsenic admits of four modifications:

1. *Reich Method Proper.*—The Ag_3AsO_4 is cupelled in a muffle with lead and the resulting silver button weighed.

2. *Pearce's Modification.*—The Ag_3AsO_4 is dissolved in nitric acid and the silver determined by Volhard's method.

3. *Author's First Modification.*—The excess of a standard solution of silver is determined by Volhard's method. By subtraction the combined silver is found, and, by calculation, the arsenic.

4. *Author's Second Modification.*—The Ag_3AsO_4 is dissolved in a few drops of dilute ammonia and the resulting solution caught, evaporated, dried, and weighed in a little, thin platinum dish. From the total weight of the Ag_3AsO_4 the arsenic is calculated.

The last method of determining the arsenic is direct, while all the others are indirect. All four methods give results of an extraordinary degree of correctness, but modifications 2 and 4 are by far the simplest, most convenient and accurate. I shall confine myself to a discussion of these two.

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[1] See Mr. Low's art. in Chem. News **48**, 85.

Solutions for Analysis.—1. 4.95 grams pure, dry arsenious oxide were oxidised with fuming nitric acid, evaporated with sulphuric acid, neutralised with ammonia and diluted to a litre. 2. 25 grams of H_2KAsO_4 were dissolved in water and diluted to two litres.

Solutions for Volumetric Work.—1. $\frac{1}{20}$ normal solution of thiocyanate of potassium.[1] 2. A saturated solution of ferric ammonium sulphate. 3. Dilute ammonia—say one of strong ammonia to ten of water.

The estimations which I here offer as a proof of the accuracy of both modifications were made as follows:

The solution was brought into a beaker, 50 cc. of water were added, the liquid was rendered slightly alkaline with ammonia, and the whole heated to boiling. More than a sufficient quantity of nitrate of silver to combine with the arsenic was then run in, the beaker was removed from the flame and its contents were rendered faintly alkaline. This last operation was accomplished by bringing the beaker under a clip burette containing the dilute ammonia, and permitting the same to drop in slowly, the contents of the glass being kept in a constant and violent state of agitation. By means of this vigorous stirring the arseniate of silver is made to coagulate and settle completely, leaving the supernatant liquid clear. As soon as a drop of the ammonia no longer produced a cloud in the clear upper stratum of liquid, and the reaction of the same was just alkaline to delicate litmus, the contents of the beaker were again well stirred and the whole was permitted to stand until cold. This cooling was generally hastened by placing the beaker in a dish of cold water. The liquid was thereupon filtered, the reddish-brown precipitate washed by decantation and (1) dissolved in pure nitric acid, ferric sulphate added, and the silver determined with $\frac{1}{20}$ normal thiocyanate of potassium according to Volhard, or (2) dissolved in a little warm ammonia, caught, evaporated, dried, and weighed in a little, thin platinum dish.

$$324Ag = 75As = 99As_2O_3 = 115As_2O_5,$$
$$463Ag_3AsO_4 = 75As = 99As_2O_3 = 115As_2O_5.$$

That the gravimetric is theoretically more accurate than the volumetric modification will be evident at a glance.

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[1] Modern system. See Clemens Winkler's little work, Die Maassanalyse nach neuem titrimetrischem System.

Determinations with First-Test Solution.

Volumetrically (Pearce).

No.	Cc. Solution.	Cc. $\frac{N}{20}$KCNS.	As.	As_2O_3.	As_2O_5.
1	5	7.45	.0186	.0245	.0285
2	5	7.4	.0185	.0244	.0283
3	5	7.4	.0185	.0244	.0283

Again:

No.	Cc. Solution.	Cc. $\frac{N}{20}$KCNS.	As.	As_2O_3.	As_2O_5.
1	10	15.05	.0376	.0496	.0577
2	10	15.05	.0376	.0496	.0577

Finally:

20 cc. solution $=$ 30.1 cc. $\frac{N}{20}$KCNS $=$ .0752 gram As $=$ .0992 gram As_2O_3 $=$ .1154 As_2O_5.

Gravimetrically (McCay).

No.	Cc. Solution.	Ag_3AsO_4.	As.	As_2O_3.	As_2O_5.
1	5	.1150	.0186	.0245	.0285
2	5	.1140	.0185	.0244	.0284
3	5	.1135	.0184	.0243	.0283

Again:

No.	Cc. Solution.	Ag_3AsO_4.	As.	As_2O_3.	As_2O_5.
1	10	.2318	.0375	.0495	.0576
2	10	.2315	.0374	.0494	.0575

Finally:

20 cc. solution $=$ .4625 gram Ag_3AsO_4 $=$ .0749 gram As $=$ .0989 gram As_2O_3 $=$ .1149 gram As_2O_5.

The arseniate of silver obtained in each of the above determinations was, after weighing, dissolved in pure nitric acid and the silver estimated with thiocyanate of potassium.

No.	Cc. $\frac{N}{20}$KCNS.	As.	As_2O_3.	As_2O_5.
1	7.50	.0188	.0247	.0287
2	7.40	.0185	.0244	.0283
3	7.50	.0188	.0247	.0287

Again:

No.	Cc. $\frac{N}{20}$KCNS.	As.	As_2O_3.	As_2O_5.
1	15.1	.0377	.0497	.0578
2	15.0	.0375	.0495	.0576

Finally:

.4625 gram $Ag_3AsO_4 = 30$ cc. $\frac{N}{20}$KCNS $=$ .0750 gram As $=$ .0990 gram $As_2O_3 =$ .1150 gram As_2O_5.

Theoretically: 5 cc. test solution $=$ .01875 gram As $=$ .02475 gram $As_2O_3 =$ .02875 gram As_2O_5.

10 cc. test solution $=$ .03750 gram As $=$ .04950 gram $As_2O_3 =$ .0575 gram As_2O_5.

20 cc. test solution $=$ .07500 gram As $=$ .09900 gram $As_2O_3 =$ .1150 gram As_2O_5.

It will at once be seen that the results obtained above agree in a very gratifying manner with those required by theory.

Determinations with Second-Test Solution.

Volumetrically (Pearce).

No.	Cc. Solution.	Cc. $\frac{N}{20}$ KCNS.	As.	As_2O_3.	As_2O_5.
1	10	20.70	.0517	.0683	.0793
2	10	20.65	.0516	.0681	.0791
3	10	20.65	.0516	.0681	.0791
4	10	20.75	0.518	.0685	.0795
5	10	20.75	.0518	.0685	.0795
6	10	20.70	.0517	.0683	.0793
7	10	20.70	.0517	.0683	.0793
8	10	20.75	.0518	.0685	.0795
9	10	20.70	.0517	.0683	.0793
10	10	20.65	.0516	.0681	.0791
11	10	20.70	.0517	.0683	.0793
12	10	20.70	.0517	.0683	.0793

Theoretically: 10 cc. $=$ 0.0521 gram As.

By Holthof's Iodine Method 10 cc. $=$ 0.0513 gram As.

Again:

No.	Cc. Solution.	Cc. $\frac{}{20}$KCNS.	As.	As_2O_3.	As_2O_5.
1	20	41.4	.1034	.1366	.1586
2	20	41.45	.1036	.1370	.1690
3	20	41.5	.1036	.1370	.1590
4	20	41.5	.1036	.1370	.1590

.1036 ÷ 2 $=$ .0518 gram. Required, .0513 gram.

It sometimes happens that the solution to be tested for arsenic contains small quantities of chlorine.[1] In this case chloride of silver will be precipitated along with the arseniate of silver, and since chloride of silver is soluble in ammonia, it is plain that an error will be introduced into the gravimetric modification. In order to steer clear of this difficulty and yet preserve the simplicity of the process, I endeavored to make nitric acid take the place of the dilute ammonia. In the former reagent arseniate of silver is readily soluble, while the chloride of silver remains upon the filter paper intact. However, upon simply evaporating the solution to dryness several times with small quantities of water, it is no easy matter to obtain a correct weight. It is invariably too high. The acid sticks to the residue most persistently. In one instance ten evaporations with small amounts of water failed to remove it all. If, however, after evaporation, the acid remaining be neutralised by moistening the residue with a few drops of dilute ammonia, it is only necessary to dry the contents of the dish on the water-bath and gently ignite in order to obtain a perfectly pure arseniate of silver.

Example.—10 cc. of first-test solution were precipitated with nitrate of silver, the precipitate was washed by decantation, filtered, and dissolved off the filter paper into a little platinum dish with a few drops of dilute nitric acid. The solution was evaporated on the water-bath, the residue moistened with dilute ammonia, dried, and gently ignited by playing the flame of a burner around the dish until the nitrate of ammonium had been volatilised. I obtained 0.2315 gram $Ag_3AsO_4 = 0.0495$ gram As_2O_3—the figures required by theory. The arseniate was dissolved in nitric acid and the solution, diluted to about 150 cc., titrated with thiocyanate. I used 15.05 cc. $\frac{N}{20}$ KCNS $=$ .1625 gram Ag $=$ .0496 gram As_2O_3.

The presence of chlorine, therefore, cannot be urged as an argument against the general use of the gravimetric modification.

The Reich method is admirably adapted for estimating arsenic in ores and metallurgical products. The method of procedure is this: The ore, speiss, matte or slag is ground to an impalpable powder and a convenient quantity weighed out in an ordinary, medium-sized platinum crucible. The crucible is then covered with a watch-glass having a hole drilled through its centre, and through this hole there are introduced into the crucible 5 cc. of dilute nitric acid. Care should be taken that the nitric acid be properly diluted, otherwise a violent reaction may ensue and some of the material be thrown out of the crucible. Heat is applied, and as soon as reaction sets in the crucible is put in a cool place and permitted to stand until the evolution of orange fumes ceases. The glass is rinsed with a few drops of water which are allowed to drain into the crucible and the solution is evaporated on the water-bath to the consistency of paste. Five to six times the weight of a mixture of four parts sodium carbonate and one part sodium nitrate are brought into the crucible and the whole is well mixed with a stout platinum wire. The substance adhering to the wire is thoroughly dried, and then, by means of a bit of broken glass, scraped back into the crucible. A little sodium carbonate is now sprinkled over the mixture, the lid of the crucible put on, and the whole gently heated by playing the flame of a burner around the crucible until all moisture is expelled. The contents of the crucible are gradually heated to fusion and kept in this state for about fifteen minutes. The fused mass is extracted with hot water, the oxides of the heavy metals are filtered off, and the filtrate is rendered weakly acid with nitric acid.[1] It is then boiled to expel carbon dioxide and evaporated to dryness. The residue is heated, taken up with water, and the solution filtered into a measuring flask. The flask is filled to the mark with water, well shaken and a convenient volume of the solution withdrawn with a pipette and treated as has been already described. If the quantity of arsenic be small, the entire solution of the alkaline arseniate is taken for analysis. The volume in this case should be equal to about 100 cc.

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[1] This is especially so in the analysis of ores and metallurgical products. The alkalies used for fusing almost always contain some chlorine.

When rapidity and not extreme accuracy is demanded, the preliminary oxidation with nitric acid as well as the subsequent evaporation of the acidified filtrate can be dispensed with. If, however, the preliminary oxidation be neglected, it will be necessary, unless the percentage of arsenic in the substance be relatively small, to employ a porcelain, iron or nickel crucible for fusion. Porcelain crucibles are never desirable, owing to the fact that the fused alkalies soon eat their way completely through the bottom. I have never been able to use a porcelain crucible for more than two or three determinations. Little wrought-iron crucibles of the size and shape of the ordinary platinum crucible are very convenient and serve the purpose well, when mere estimations of arsenic are under consideration. Nickel crucibles would, doubtless, prove quite practical, but I have thus far had no experience in using them. Rose says that platinum crucibles are seriously damaged by the joint action of the molten alkali arseniates and the gas of the lamp. Fresenius appears to share Rose's opinion. My experience has been that the crucibles suffer to a far less degree than was formerly supposed. I have used a little platinum crucible over and over again for the fusion of ores, some of which have contained as much as 50 per cent. arsenic, but it does not appear to have undergone any definite injury. When an ore is rich in arsenic I generally use 0.1–0.25 gram; sometimes, however, as much as 1.0 gram is taken for analysis. There is, indeed, an action of the alkali upon the platinum, but, taking everything into consideration, it is insignificant. A crucible, before the fusion of 0.25 gram nickel speiss containing 51.25 per cent. arsenic, weighed 21.2620 grams and, after fusion, 21.2608. The difference is 0.0012 gram. Even carbonates of the alkalies attack platinum to this extent. Dr. L. de Koninck[1] found that a crucible in which he had fused 6 grams potassium sodium carbonate lost 0.001 gram.

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[1] Since acetate of sodium serves in a remarkable manner to promote the separation of the arseniate of silver, it might be well to substitute acetic for nitric acid. See Charles E. Avery, Sill. Am. J. [2], **47**, 25.

I have selected the following examples from a large number of analyses, inasmuch as they seem peculiarly suited for giving the practical chemist a general idea as to the most convenient quantities of material to be taken for analysis, as to the volumes of $\frac{1}{20}$ normal thiocyanate to be expected, and as to the agreement of duplicate tests.

I.—*Lead Matte.*[2]

	Grams Substance.	Cc. $\frac{1}{20}$ Normal KCNS.	Per cent. As.
1	0.9983	7.3	1.83
2	0.9980	7.4	1.85

II.—*White Iron.*[2]

	Grams Substance.	Cc. $\frac{1}{20}$ Normal KCNS.	Per cent. As.
1	1.0023	25.35	6.32
2	1.0075	26.0	6.45

III.—*Lead Speiss.*[2]

	Grams Substance.	Cc. $\frac{1}{20}$ Normal KCNS.	Per cent. As.
1	0.9985	38.7	9.71
2	0.9974	38.4	9.63

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[1] Zeits. für analy. Chem. **18**, 569.

[2] Analysed by Mr. J. W. Phillips.

IV.—*Nickel Speiss.*

1.0 gram was oxidised, fused, and extracted with hot water; the solution was filtered into a 500 cc. flask, acidified with nitric acid, boiled, cooled, and diluted to the mark. The flask was well shaken and for each estimation 50 cc. taken.

	Cc. Solution.	$\frac{1}{20}$ Normal KCNS.	Per cent. As.
1	50	20.55	51.36
2	50	20.45	51.12
3	50	20.45	51.12
4	50	20.50	51.25

1.0 gram speiss + 0.3 gram Sb_2O_3 was oxidised, fused, and extracted with hot water; the solution was *cooled*, filtered into a 500 cc. flask, acidified with a little nitric acid, boiled, cooled, diluted to the mark and well shaken. When the liquid had cleared the following determinations were made:

Volumetrically.

	Cc. Solution.	$\frac{1}{20}$ Normal KCNS.	Per cent. As.
1	50	20.5	51.25
2	50	20.45	51.12

Gravimetrically.

Cc. Solution.	Grams Ag_3AsO_4.	Per cent. As.
50	.317	51.35

The .317 gram Ag_3AsO_4 was dissolved in nitric acid and titrated. I used 20.5 cc. $\frac{1}{20}$ normal KCNS = 51.25 per cent. As.

These determinations show conclusively that antimony is without influence. By far the greater portion remains behind with the metallic oxides as sodium metantimoniate. The very small amount which goes into solution is precipitated by the nitric acid and, upon permitting the liquid to stand, separates as a heavy white powder. 50 cc. of the above solution were mixed with 5 cc. strong sulphuretted hydrogen water. The liquid remained perfectly clear and limpid for at least five minutes. The subsequent appearance of a faint opalescence, which gradually increased in intensity, plainly indicated a reduction of arsenic from the maximum to the minimum state of oxidation. Had even a trace of antimony been present, it should have been immediately precipitated by the sulphuretted hydrogen. Numerous examples could be given showing that antimony exerts no influence, but these determinations will doubtless suffice.

Certain acid-forming oxides, such as those of phosphorus, molybdenum and vanadium, interfere with the determination of the arsenic. If any or all of these oxides be present, the arsenic must be precipitated as sulphide, then oxidised and fused.

In laboratories where large numbers of arsenic determinations are being constantly made, Mr. Pearce's volumetric modification of the Reich method will be found most practical; in laboratories, however, where there is only occasionally a demand for an arsenic determination, the author's gravimetric modification will prove most convenient.

In closing I should like to suggest that, while due allowance be made for the modifications, this silver process be henceforth known as the Reich method for determining arsenic.

JOHN C. GREEN SCHOOL OF SCIENCE, PRINCETON, N. J., *March* 1, 1886.

Communication from the Chemical Laboratory of Rutgers College.

XIII.—ON DINITROSULPHOCYANBENZENE.

BY PETER T. AUSTEN AND FRANKLIN S. SMITH.

Clemm[1] found that when trinitrochlorbenzene was treated with potassium sulphocyanide an energetic action ensued and a well-characterised compound was formed. He was unable, however, even after a number of analyses, to assign any satisfactory formula to this substance.

It appeared probable that the dinitro-derivative would be less likely to cause the formation of secondary reactions, and, if this were the case, a dinitrosulphocyanbenzene would be created. It was found on experiment that the reaction did take place easily and in quite quantitative relations.

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[1] Journ. prakt. Chem. [2], **1**, 145.

Dinitrobrombenzene was dissolved in methyl alcohol, and about half its weight of potassium sulphocyanide added. The flask was placed on a water-bath and connected with a return condenser. After boiling a short time the precipitation of a yellow, crystalline sand begins, the amount of which continually increases. To avoid the excessive bumping which soon takes place, it is well, at intervals, to pour off the liquid, remove the sand, and begin the boiling anew. After an hour's boiling but little more precipitation takes place. The sand should then be removed and the liquid distilled down about one-half. On boiling the remaining liquid as before, a fresh deposit of sand will take place. In this manner a very satisfactory yield is obtained. The liquid shows a strong reaction for bromides as soon as this precipitation of the sand begins.

Dinitrosulphocyanbenzene.

The yellow sand obtained by the method just described was well washed with boiling methyl alcohol to remove any traces of the dinitrobrombenzene, and then repeatedly boiled out with water until free from bromides. When dry the substance is a fine sand, which consists of yellow, crystalline, transparent grains. It is moderately soluble in boiling chloroform, which is the best solvent which we have yet been able to find for it. Crystallised from chloroform it forms buff-yellow, small, hard, transparent crystals fusing at 139°.

Analysis:

$C_6H_3(NO_2)_2SCN$.	Calculated.	I.	II.
C	37.33	37.12	37.43
H	1.33	1.51	1.37
N	18.66	18.24	18.06
S	14.22	14.43	...

The substance is reduced with difficulty by tin and hydrochloric acid. The resulting base was not examined. The substance was slowly dissolved by concentrated boiling caustic soda, but no definite compound could be isolated from the resulting solution.

Dinitrophenylmercaptan.

When dinitrosulphocyanbenzene is added to an excess of concentrated sulphuric acid and the mixture gently heated, the reaction begins and the temperature rises, while large amounts of sulphur dioxide and carbon dioxide are evolved and ammonium sulphate is formed in the solution. The substance, which at first goes into solution in the acid, is reprecipitated. The resulting liquid and precipitate were allowed to cool somewhat and then poured carefully into a sufficient volume of cold water. The precipitate was filtered off and washed with hot water till no reaction for sulphuric acid was obtainable. As we were unable to find any solvent for this substance from which we could crystallise it (even nitrobenzene failing to give satisfactory results), we proceeded to purify by repeated extractions with boiling alcohol, and lastly with boiling chloroform. The compound obtained after drying is an impalpable, light yellow powder. It is extremely adherent to glass, which makes it rather difficult to transfer it from one vessel to another, and it is also not easy to obtain it perfectly free from moisture.

$C_6H_3(NO_2)_2SH$.	Calculated.		
C	36	35.50	35.50
H	2	2.66	2.17
N	14	14.40	...
S	16	15.57	...

The substance is insoluble in the usual solvents. Nitrobenzene dissolves small amounts of it, but we were unable to obtain it again in a crystalline condition. It dissolves easily in warm, concentrated nitric acid, and is precipitated unchanged on pouring the solution into cold water. It fuses at 195°, and on heating it deflagrates.

We were somewhat at a loss at first to understand the reaction taking place here, but on comparing it with the action of concentrated hydrochloric acid under pressure on sulphocyanbenzene,[1] the mechanism of it was at once apparent.

$$C_6H_5SCN + 2H_2O = C_6H_5SH + CO_2 + NH_3,$$
$$C_6H_3(NO_2)_2SCN + 2H_2O = C_6H_3(NO_2)_2SH + CO_2 + NH_3.$$

The evolution of sulphur dioxide is probably due to a secondary action. If the action is continued too long, or the heat is raised too high, the substance is decomposed, and the compound is not obtained.

Dinitrophenylsulphide.

When dinitrosulphocyanbenzene is added to a mixture of fuming nitric acid and concentrated sulphuric acid, and the whole warmed, an energetic action takes place. The resulting solution was poured into water, and the white, flocculent precipitate which separated, was washed out with boiling water and dried. It formed a grayish-white mass with a very irregular fracture. It dissolved in boiling glacial acetic acid with some difficulty, but more easily when it was well rubbed with the acid in a mortar so as to remove the adhering film of air. From this solution it crystallised in beautiful, transparent, slightly yellow needles nearly a quarter of an inch long and about as thick as a pin, forming fan and stellar aggregates and fusing at 245°.

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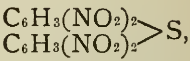
[1] Billeter. Ber. **7**, 1753.

Analysis gave—

$(C_6H_3(NO_2)_2)_2S$.	Calculated.	Found.
C	39.34	39.20
H	1.64	1.57
N	15.30	15.38
S	8.74	8.82

The substance is then dinitrophenylsulphide,



$\begin{matrix}C_6H_3(NO_2)_2\\C_6H_3(NO_2)_2\end{matrix}>S$,

and is hence isomeric with the one discovered by Beilstein and Kurbatow.[1]

A LECTURE EXPERIMENT FOR SHOWING THE COMPOSITION BY VOLUME OF NITROUS AND NITRIC OXIDES.

By E. H. Keiser.

The usual method of showing that nitrous oxide contains its own volume of nitrogen, and that nitric oxide contains half its volume of nitrogen, is to decompose these gases by bringing them in contact with heated potassium. For this purpose a quantity of the gas to be examined is collected in a eudiometer over mercury, and its volume is determined. The gas is then transferred to a bent glass tube closed at one end, and a small piece of potassium is introduced into the bent portion of the tube by passing it up through the mercury by means of a wire. The lower and open end of the tube is now closed under the mercury with the finger, and the part of the tube containing the potassium is heated with the lamp. After the combustion the tube is allowed to cool. The gas, which now consists of nitrogen, is transferred back again to the eudiometer, and its volume is determined. To perform this experiment successfully, considerable skill in the manipulation of gases is necessary, and it requires so much time that it is not adapted to the purposes of the lecture table.

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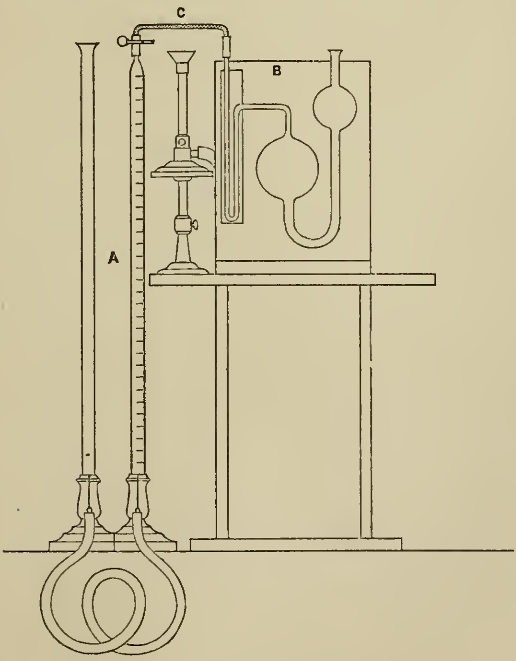
[1] Ann. d. chem. Pharm. **197**, 77.

The same object may be attained much more easily and rapidly by means of the simple apparatus shown in the cut. It is based upon the fact that heated metallic copper combines with all the oxygen of the nitrogen oxides and sets the nitrogen free. The method of using the apparatus is very simple, and requires but little explanation. *A* represents a gas burette for measuring the volumes of the gases. *B* is a gas pipette, which is filled with water.



The connecting tube *C* is made of hard glass and is 3 mm. internal diameter, and from 10 to 12 cm. long. It is completely filled with granular metallic copper, which has been obtained by the reduction of the granular oxide in a current of hydrogen. The copper is held in place by plugs of asbestos in each end of the tube. To decompose the oxides of nitrogen, this tube is heated to a red heat with a Bunsen burner, and to prevent it from bending, a piece of wire gauze is wrapped around the outside and secured by wires.

A measured quantity of nitrous or nitric oxide contained in the burette *A* is passed over the heated copper by opening the pinch-cock and raising the reservoir tube of the burette. When the reservoir tube is lowered, the gas is drawn back from the pipette. It now consists of nitrogen, and its volume may be readily determined. If nitric oxide has been used, the volume of nitrogen obtained will be exactly one-half the original volume of the gas, while in the case of nitrous oxide the volume of nitrogen will be the same as the volume of nitrous oxide taken, although the copper will have been oxidised and the gas will have lost its power of supporting combustion. The error rarely exceeds .1 per cent. in the case of nitric oxide, while with nitrous oxide equally good results are obtained if the water in the burette has been previously saturated with the gas.

It is of course necessary to have the oxides of nitrogen free from air. The burette may be conveniently filled with pure nitric oxide as follows: Into a flask of about 300 cc. capacity there is placed a mixture of 100 grams of ferrous sulphate and 12 grams of potassium nitrate. To this is added a quantity of dilute sulphuric acid, obtained by mixing 60 cc. of the concentrated acid with 160 cc. of water. The flask is closed with a one-hole rubber stopper, through which passes a glass tube bent at right angles. On heating the mixture contained in the flask pure nitric oxide is evolved. A T tube is then attached to the gas burette, and one of its branches is connected with the outlet tube of the flask. The air in the burette is expelled by opening the pinch-cock and raising the reservoir tube until water flows out of the open end of the T tube. After all the air has been expelled from the generating flask the open end of the T tube is closed with a rubber tube and pinch-cock, and the gas allowed to pass into the burette.

The same apparatus serves for filling the burette with nitrous oxide, the gas in this case being made by heating pure ammonium nitrate.

BRYN MAWR, PA., *February*, 1886.

SUBSTITUTION PRODUCTS OBTAINED FROM SALICYLIC ACID.

By Edgar F. Smith and E. B. Knerr.

The mono- and di-halogen substitution products of salicylic acid have been pretty thoroughly studied, so that it may seem unnecessary to carry investigation any further in that direction. We have, however, obtained several new di-halogen acids and their derivatives by introducing two different halogen atoms into salicylic acid. These are of interest, and below we give one of these acids, reserving the others for a future communication.

1. *Meta-chlor-iodo-salicylic acid*, $C_6H_2(OH)Cl.I.COOH$.—This acid we obtained from the chlorsalicylic acid melting at 172° C. We first endeavored to prepare it by dissolving the chlorsalicylic acid in alcohol and adding the calculated amount of iodine. In one instance heat was applied to the solution. After standing for several hours the alcoholic liquid was transferred to a porcelain dish and evaporated to dryness. The residual mass was converted into the barium salt, which separated from the concentrated aqueous solution in arborescent crystals, resembling those of barium dichlorsalicylate. The salt was recrystallised and then analysed.

.1235 gram air-dried salt, heated to 160° C. for two hours, lost .0112 gram H_2O, equivalent to 9.06 per cent. H_2O.

The found $BaSO_4$ equalled .0373 gram $Ba = 17.73$ per cent. Ba.

An analysis of a barium salt obtained in the same manner, but at another time, gave a like result. These results point to the conclusion that the salt analysed was that of a chlor-iodo-benzoic acid, and not the barium salt of chlor-iodo-salicylic acid.

Barium chlor-iodo-benzoate, $(C_6H_3Cl.I.COO)_2Ba + 4H_2O$, requires 17.70 per cent. Ba and 9.30 per cent. H_2O. We found 17.73 per cent. Ba and 9.06 per cent. H_2O. The acid from the salt mentioned above is quite soluble in boiling water. It forms curved needles, melting at 210°C.

By pursuing the method recommended by Weselsky[1] for the introduction of iodine into aromatic compounds—viz.: the addition of mercuric oxide together with iodine to the alcoholic solution of chlorsalicylic acid, the chlor-iodo acid was obtained easily and in good quantity. The reaction was aided by a gentle heat, and when completed, the alcoholic solution was evaporated to dryness, the residue boiled up with an excess of sodium carbonate, and the liquid filtered. The discolored filtrate was acidified with hydrochloric acid and the acid, which separated, was filtered off, washed, and converted into a barium salt. The latter separated from its concentrated aqueous solution in bundles of needles having a pink color. This salt was recrystallised six times. The acid from it was also recrystallised a number of times, and its melting-point tested on each occasion. It melted regularly at 224° C., with slight decomposition. The acid is difficultly soluble, even in boiling water. From a mixture of hot water and alcohol it separates in long, colorless needles. Ferric chloride imparts a violet coloration to its solutions. After proving the presence of both iodine and chlorine qualitatively, the acid was burned, together with lead chromate.

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[1] Ann. **174**, 99.

.3080 gram dried acid gave .0852 gram carbon = 27.66 per cent. C, and .0059 gram hydrogen = 1.59 per cent. H.

The acid $C_6H_2(OH)Cl.I.COOH$ requires 28.13 per cent. carbon and 1.34 per cent. hydrogen.

Theoretically, this acid contains 42 per cent. of iodine, and in its combustion, as well as in that of the ethyl ester (see below), this high iodine content gave us trouble, as free iodine invariably escaped from the combustion tube and settled in the calcium chloride tube. To obviate this we resorted to the following expedient: after filling the tube with a long layer of lead chromate we placed upon the latter a wad of asbestos, following this with a layer of the same material charged with metallic silver, which we deposited by the electric current. The silvered asbestos was heated, and effectually prevented the iodine vapors from entering the calcium chloride tube. A layer of metallic silver (from the oxide) answered the same purpose.

Salts of Chlor-iodo-salicylic Acid.

Sodium Chlor-iodo-salicylate, $C_6H_2(OH)Cl.I.COONa + 2H_2O$, was made by boiling the acid with sodium carbonate. It is soluble in water and crystallises from the same in beautiful, flat, shining needles, which in several instances exceeded an inch in length.

Analysis: .1607 gram air-dried salt lost on heating to 150° C. for several hours, .0184 gram H_2O = 10.76 per cent., equivalent to

2 mols. The sodium sulphate weighed .0315 gram = .0102 gram Na, equivalent to 6.34 per cent. Na. Theory requires 10.09 per cent. H_2O and 6.45 per cent. Na.

Calcium Chlor-iodo-salicylate, $(C_6H_2.OH.Cl.I.COO)_2Ca + 5H_2O$.—This salt consists of beautiful pink needles. It is much more soluble in water than the corresponding barium salt.

Analysis: Found 13.32 per cent. H_2O and 5.54 per cent. Ca. Required 12.41 per cent. H_2O and 5.51 per cent. Ca.

Barium Chlor-iodo-salicylate, $(C_6H_2.OH.Cl.I.COO)_2Ba + 4\frac{1}{2}\ H_2O$.—It occurs in long pink needles, rather difficultly soluble in water.

Analysis: .1582 gram salt lost, at 180° C., .0151 gram water = 9.54 per cent., or 4½ mols. The $BaSO_4$ equalled .0436 gram = .0256 gram Ba, or 16.18 per cent. Required 9.96 per cent. H_2O and 16.83 per cent. Ba.

Magnesium Chlor-iodo-salicylate, $(C_6H_2.OH.Cl.I.COO)_2Mg + 5\frac{1}{2}H_2O$.—Pink leaflets, quite soluble in hot water. Its analysis gave the following:

.4023 gram substance heated to 135° C. to constant weight lost .0558 gram = 13.87 per cent. H_2O, equivalent to 5½ mols.

The magnesium which was found equalled 3.83 per cent. Theory requires 13.78 per cent. H_2O and 3.87 per cent. Mg.

Zinc Chlor-iodo-salicylate, $(C_6H_2(OH)I.Cl.COO)_2Zn + 3H_2O$.—Beautiful white needles, grouped together in clusters. It is quite readily soluble in hot water.

Analysis: .1888 gram substance lost .0144 gram when heated to 130° C. This is equivalent to 7.62 per cent. H_2O, or 3 mols.

The quantity of ZnO equalled .0214 gram = .0170 gram Zn or 9.00 per cent. Zn. Theory requires 7.57 per cent. H_2O and 9.10 per cent. Zn.

The following salts were prepared, but not analysed: the *potassium* salt, forming reddish-brown, matted needles, quite soluble in water; the *manganese* salt, consisting of chocolate-brown monoclinic needles, readily soluble in water; the *cadmium* salt, appearing in pink needles, which are rather soluble; the *silver* salt, forming an amorphous, yellow, insoluble powder; and the *copper* salt, consisting of bluish-green soluble needles.

Esters of Chlor-iodo-salicylic Acid.

The *methyl ester*, $C_6H_2.OH.Cl.I.CO.O.CH_3$, was prepared by heating the silver salt with alcoholic methyl iodide in a flask provided with a return cooler. The compound separated from its concentrated alcoholic solution in flat, broad needles, melting at 129°–130° C.

The *ethyl ester*, $C_6H_2.OH.Cl.I.CO.O.C_2H_5$, forms white plates, readily soluble in hot alcohol. It was analysed as indicated under the acid.

Analysis : .1427 gram dry substance gave .0475 gram carbon = 33.28 per cent. C, and .0044 gram H = 3.08 per cent. H. Theory requires 33.07 per cent. C and 2.45 per cent. H.

Some years ago a dichlorsalicylic acid was prepared by one of us (S.). At that time but one acid of this description was known.[1] The acid of Rogers melted at 223°–224°, while the one obtained by us melted at 213°–214° C. Points of difference in various salts were also observed, so that a number of these, as well as other derivatives, were made and analysed.[2] We have had occasion to repeat our work with the dichlor-acid, and have gotten results agreeing with those obtained at first. The melting-point of the acid has been repeatedly tested and found to be 213°–214°. This acid we have endeavored, by various ways, to convert into a dichlor-nitro-salicylic acid, but have not succeeded. The first attempt was made by dissolving the dichlor-acid in a cooled mixture of equal parts of fuming nitric acid and glacial acetic acid. On pouring the solution into water a yellow-colored mass separated. This was filtered, washed with cold water, and then converted into a barium salt. As the aqueous solution cooled the salt separated out in orange-colored needles. It dissolved with difficulty, even in hot water. After several crystallisations it was analysed.

.1626 gram air-dried salt lost, at 180° C., .0088 gram H_2O = 5.41 per cent. ; the $BaSO_4$ weighed .0645 gram = .0379 gram Ba, or 23.30 per cent. Ba.

These results indicate a dichlornitrophenol. The free phenol from the above salt is very difficultly soluble in hot water. It volatilises with steam and crystallises in yellow-colored leaflets melting at 122° C. By reference to the first edition of Beilstein's Org. Chemie, p. 1022, it will be noticed that three phenols of the constitution indicated by the above analysis exist, and that the 1, 2, 4, 6-body melts at 121°–122° C., forms yellow leaflets, and further, that its barium salt consists of bundles of orange-red needles, difficultly soluble in water. The salt also contains two mols. of H_2O. Our salt fully agrees with all these properties. The potassium salt obtained by us formed chrome-red, anhydrous, flat needles. This, too, agrees with the potassium salt of the 1, 2, 4, 6-phenol.

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[1] Rogers, Inaugural Diss. Goettingen, 1875.

[2] Beilstein's Organische Chemie, Erste Aufl.

Our other attempts to introduce the nitro-group into the dichlor-acid were made by taking, first, two parts of glacial acetic acid and one part nitric acid; second, by conducting the vapors from lead nitrate into a glacial acetic acid solution of the acid; and third, by leading the gas evolved from the action of nitric acid and arsenious acid into an ethereal solution of the dichlor-acid. The principal product in all these experiments was the dichlor-nitrophenol melting at 122°.

Upon fusing dichlorsalicylic acid with potassium hydroxide we obtained a product which in many respects indicated gallic acid. The true position of the second atom of chlorine in the dichlor-acid melting at 213°–214° has never been definitely determined.

Action of the Gas from As_2O_3 *and* HNO_3 *upon Wintergreen Oil.*

At the suggestion of one of us (S.) Mr. A. F. Linn, formerly of this laboratory, rectified a quantity of commercial wintergreen oil, and, after dissolving a portion of the purified product in ether, conducted the gas obtained from arsenious oxide and nitric acid into the ethereal solution, until it had assumed a deep reddish-brown color. The vessel containing the mixture was cooled as long as the gas was introduced, but then tightly corked and gently warmed upon a water-bath for a brief period, after which it was allowed to stand. In the course of a few hours a mass of crystals separated. These were removed and, after being freed of adhering oil, were digested with hot ether. It was soon observed that a part of the crystalline mass was exceedingly insoluble in the solvent employed. This suggested treating the compound, finely divided, first with cold ether. By this procedure the original product was resolved into two portions, the one quite readily soluble in cold ether, the other only soluble in this reagent when it was applied warm and in considerable quantity. The soluble compound, after a number of crystallisations, showed the constant melting-point

94°. It forms long, white needles. For convenience we will designate it *A*. The insoluble derivative, which we will call *B*, crystallised from ether in octahedral forms, exhibiting a beautiful play of colors. It melted at 118° C. At this point Mr. Linn discontinued the work. We have since obtained the same compounds, and our first step was to expose them to the action of boiling alkaline hydroxides. After treating *A* several hours with potassium hydroxide its cold solution was acidified with hydrochloric acid, which caused the separation of a white, flocculent mass. This was filtered, washed with cold water, and then converted into a barium salt. A portion of the free acid melted at 227°–228° C. Its fusion at this temperature, and the manner in which it had been obtained, led to the suspicion that the acid was, in all probability, α-metanitrosalicylic acid (m. p. 228° C.)[1] We therefore set free all the acid from the barium salt and converted it into the corresponding calcium salt. This we obtained in long, delicate, silky needles. It was analysed.

.1340 gram air-dried salt lost, at 180° C., .0276 gram water, or 20.58 per cent. H_2O.

The $CaSO_4$ found weighed .0358 gram, equivalent to .0104 gram $Ca = 9.77$ per cent. Ca.

This salt is very readily soluble, even in cold water. By reference to the articles already cited it will be discovered that the properties of the salt analysed by us agree perfectly with those of the calcium salt of α-metanitrosalicylic acid, and that the analysis just given agrees with the theoretical requirement of the salt $(C_6H_3(NO_2)OH.COO)_2Ca + 6H_2O$. The free acid gave a deep blood-red color with ferric chloride; this is also a characteristic of the nitrosalicylic acids. As already observed, the acid melted from 227°–228° C. The compound affording the α-nitro-acid melted at 94° C. Assuming this to be the ethyl ester of the acid, it will be noticed, on reference to Wattenberg's thesis, that the ethyl ester prepared by him melted at 93° C.; further, that the properties of the two compounds are identical. They are doubtless the same.

The insoluble product *B* was likewise boiled with potassium hydroxide. The acid from it appeared to be more soluble than the acid derived from *A*. It was, however, converted into its barium salt. This crystallised in rather large, yellow-colored needles from its dilute aqueous solution. An analysis of the salt gave the following:

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[1] Wattenberg's Inaugural Dissert. Goettingen, 1875; and Ann. **195**, 9.

.1708 gram air-dried salt suffered no loss on heating it to 150° C. for several hours. Evaporated to dryness with sulphuric acid it gave .0788 gram $BaSO_4$ = .0463 gram Ba = 27.10 per cent. Ba.

This agrees with the requirements of an anhydrous barium nitrosalicylate, which demands 27.20 per cent. Ba. The salt corresponds to that described by Hall.[1] The acid, after several crystallisations, melted at 125° C., and when anhydrous, at 144° C., proving conclusively that it was β-metanitrosalicylic acid. Ferric chloride imparted a blood-red coloration to its aqueous solution. The compound *B* melting at 118° C. we have not investigated farther.

The production of the two isomeric nitrosalicylic acids by the above method is new, so far as we are aware; hence this detailed account.

WITTENBERG COLLEGE, SPRINGFIELD, OHIO, *March* 2, 1886.

ON BENZOYLACETIC ACID AND SOME OF ITS DERIVATIVES.[2]

PART IV.

BY W. H. PERKIN, Jun., *Privatdocent at the University of Munich.*

(Continued from p. 372, Vol. 7.)

Dehydrobenzoylacetic Acid.

Among the many reactions in which ethylic acetoacetate takes part, there are few more interesting than the condensation which this body undergoes on prolonged boiling; by this treatment two molecules appear to combine, with elimination of two molecules of alcohol and formation of dehydracetic acid, according to the equation—

$$2CH_3.CO.CH_2.COOC_2H_5 = C_8H_8O_4 + 2EtOH.$$

This acid, the constitution of which, in spite of many experiments, still remains to be explained, was first obtained by Geuther[1] by passing carbonic anhydride over the heated sodium derivative of ethylic acetoacetate. During the reaction a quantity of ethylic acetoacetate distils over, and the sodium salt of dehydracetic acid remains in the retort. On dissolving the latter in water and acidifying with dilute sulphuric acid the acid is set free, and by repeated recrystallisation from water, can easily be obtained pure in colorless leafy crystals melting at 109°.

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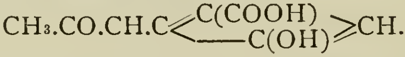
[1] Dissertation, Goettingen, 1875; and Ann. **195**, 31.

[2] Communicated by the Author.

Geuther proved this compound to be a monobasic acid, forming salts of the formula $C_8H_7O_4M$. At a more recent date Oppenheim and Precht[2] undertook the further investigation of the acid, and succeeded in preparing a number of derivatives, which they carefully examined, and from the results proposed the following as the most probable constitutional formula:



$$\mathrm{CH_3.CO.CH.C}{<}\begin{matrix}\mathrm{C(COOH)}\\ \mathrm{C(OH)}\end{matrix}{>}\mathrm{CH.}$$

This formula presupposes that in the formation of this acid from two molecules of the acetoacetate, the methyl-group of one molecule takes part in the reaction, whereas the methyl-group of the second molecule remains intact. In order to test the accuracy of this formula it appeared interesting to determine whether it would be possible under the same conditions to obtain a similar body from ethylic benzoylacetate, in which case the two phenyl-groups would be excluded from taking part in the condensation.

The constitution of an aromatic compound of this kind would probably be much easier to determine, and if it were found that its derivatives behaved in a way exactly analogous to those of dehydracetic acid itself, it would be legitimate to suppose that the methyl-groups of the two molecules of ethylic acetoacetate which went to form dehydracetic acid did not take part in the reaction.

In the first experiments on ethylic benzoylacetate it was noticed that in distilling this body rapidly a great part went over as a colorless oil, a considerable quantity of a black tarry mass being left behind, partly soluble in carbonate of soda solution on continued agitation. On filtering and acidifying the alkaline solution an acid was deposited in the form of brownish flakes; this by repeated recrystallisation from alcohol was obtained pure in the form of long yellow needles. As it was thought possible that this might be the desired acid, numerous experiments were made in order to find some means of obtaining it in larger quantity. The following process was found to give the best results:

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[1] Zeitschrift für Chemie, 1866, 8.

[2] Berichte **9**, 324, 1100.

Ethylic benzoylacetate was first heated to boiling in portions of 10–15 grams in test-tubes or small retorts for 7–8 minutes, during which operation the mass gradually became darker, whilst a quantity of lower boiling oil was given off; this was collected for further examination. On cooling, the residue generally solidified to a brownish cake of crystals. The distillate from a number of such operations was first examined. On fractioning, the principal portion passed over between 70° and 110°, then the thermometer rose rapidly to 180°, between which temperature and 210° a considerable quantity distilled; a small residue was left, which appeared to consist in great part of unchanged ethylic benzoylacetate. The fraction 70°–110°, which had a strongly acid reaction, was mixed with dry carbonate of potash, and after remaining for some time, distilled on a water-bath. On further fractioning, the distillate went over almost to the last drop between 78° and 80°, and possessed all the properties of common alcohol. The residual potash salt was then acidulated with dilute sulphuric acid and distilled in steam; a strongly acid liquid passed over, which showed all the reactions of acetic acid. The fraction 70°–110° was therefore a mixture of alcohol and acetic acid.

On refractioning the fraction 180°–210°, nearly the whole distilled over between 190°–200°, and was from its odor easily recognised as acetophenone. This was confirmed by warming it with a solution of orthonitrobenzaldehyde in dilute sodic hydroxide, when a copious precipitate of indigo was slowly formed.

The solid residue from these experiments was then boiled for a considerable time with alcohol and animal charcoal, and filtered, the new acid crystallising out in long yellow needles on cooling. On distilling off the alcohol from the mother-liquor of these crystals it deposited a quantity of a dark brown oil; on heating this again in the way described above, it gave a new quantity of acid. This treatment was repeated until the residual oil on further heating no longer solidified on cooling, but remained behind as a blackish tarry mass, which, however, still contained considerable quantities of the acid. In order to extract this, the whole was dissolved in a little alcohol, enough potash added to neutralise the acid, the product diluted with water, and several times extracted with ether. On acidifying the solution of the potash salt, the acid was deposited in a crude state, and was treated with alcohol and animal charcoal as described above.

The different crops of crystals were then mixed together, crystallised several times from alcohol, and thus obtained pure. The analysis gave the following numbers:

I. 0.1879 gram substance gave 0.0715 gram H_2O and 0.5082 gram CO_2.

II. 0.2577 gram substance gave 0.0958 gram H_2O and 0.6978 gram CO_2.

III. 0.1941 gram substance gave 0.0746 gram H_2O and 0.5241 gram CO_2.

IV. 0.1974 gram substance gave 0.0740 gram H_2O and 0.5319 gram CO_2.

	Found.				Theory, $C_{18}H_{12}O_4$.
	I.	II.	III.	IV.	
C	73.76	73.85	73.64	73.49 per cent.	73.97 per cent.
H	4.22	4.13	4.27	4.16	4.11
O	22.02	22.02	22.09	22.35	21.92

This substance, for which I propose the name dehydrobenzoylacetic acid, has therefore the formula $C_{18}H_{12}O_4$, and is formed from two molecules of ethylic benzoylacetate in a way exactly analogous to the formation of dehydracetic acid from ethylic acetoacetate, according to the equation—

$$\underset{\text{Ethylic benzoylacetate.}}{2C_6H_5.CO.CH_2.COO.C_2H_5} = \underset{\text{Dehydrobenzoylacetic acid.}}{C_{18}H_{12}O_4} + 2C_2H_5.OH.$$

This acid crystallises from its solution in hot alcohol in long yellow needles which melt at 171°–172°. It is moderately soluble in hot alcohol, but only sparingly in the cold. On the addition of a drop of ferric chloride to the hot alcoholic solution it gives a deep orange-red coloration. Dehydrobenzoylacetic acid dissolves easily in benzene, chloroform, bisulphide of carbon and ether, but sparingly so in light petroleum. On evaporating these solutions the acid crystallises out beautifully in long yellow needles. The solution in bisulphide of carbon does not decolorise bromine in the cold, and only very slowly on boiling, hydrogen bromide being given off. This behavior is exactly analogous to that of dehydracetic acid, which, when treated with bromine, forms a substitution-product, $C_8H_7O_4Br$, and not an additive product, as might be expected, considering the small percentage of hydrogen which the acid contains.

Dehydrobenzoylacetic acid dissolves in concentrated sulphuric acid with an olive-green color; on warming, a beautiful violet solution is obtained, which, when examined with the spectroscope, gives exactly the same absorption-spectrum as indigo.

The acid is not acted on, even by prolonged heating with acetic anhydride, being precipitated unchanged on adding water, a proof that the dehydrobenzoylacetic acid contains no hydroxyl-groups.

The acid chars when submitted to dry distillation, a quantity of gas being given off; but if heated with soda-lime, acetophenone is formed.

Dehydrobenzoylacetic acid readily combines with phenylhydrazine, forming an intensely yellow compound, which is difficult to purify, and has not as yet been analysed. The pure acid dissolves easily in ammonia, soda and sodic carbonate, forming yellow solutions.

The ammonium salt was obtained in the usual way, by allowing the solution of the acid in ammonia to stand over sulphuric acid in a vacuum until the excess of alkali had been removed. The following salts were prepared by precipitation: Silver nitrate causes the precipitation of the silver salt as a yellowish-white flocculent mass, which is very stable and only slowly acted on by light. It was collected, well washed with water, dried at 100°, and analysed with the following result:

0.2949 gram substance gave 0.0818 gram H_2O, 0.5874 gram CO_2 and 0.0786 gram silver.

	Found.	Theory, $C_{18}H_{11}O_4Ag$.
C	54.32 per cent.	54.19 per cent.
H	3.08	2.75
Ag	26.65	27.00
O	15.95	16.06

Dehydrobenzoylacetic acid is therefore a monobasic acid. The *ferric salt* is thrown down as a beautiful scarlet precipitate on adding ferric chloride to a solution of the ammonium salt. Ferrous sulphate, on the contrary, gives a blackish-violet precipitate, the behavior with these two reagents being a very characteristic reaction for the acid. The *copper salt* is obtained, on adding cupric sulphate, as a light greenish precipitate, soluble in ammonia. The *lead*, *calcium*, *barium*, *zinc* and *tin salts* are heavy white precipitates, almost insoluble in water. *Nickel sulphate* gives, with a solution of the ammonium salt, a light green almost colorless precipitate, soluble in ammonia. All these salts are extremely stable.

If ethylic benzoylacetate is boiled as described above for about eight minutes, the only condensation-product formed in any quantity is dehydrobenzoylacetic acid. If, however, the boiling is continued for a longer time, the reaction becomes more and more complicated, higher condensation-products being formed.

In order to study these, and, if possible, to determine their constitution, the ethylic benzoylacetate was heated in small retorts in quantities of from 10 to 15 grams for about half an hour, during which time alcohol and acetophenone were given off continuously and fairly regularly. The black tarry residue, which became semi-solid on cooling, was found to contain at least two condensation-products besides dehydrobenzoylacetic acid; these were separated as follows: In order to remove the dehydrobenzoylacetic acid the mass was first treated with a moderately concentrated solution of ammonia and allowed to stand, the whole being well stirred from time to time. After filtering off the aqueous solution of the ammonium salt the residue was well washed with water, and then several times extracted with hot alcohol; this removed all the coloring matter, and left a yellowish amorphous mass, which will be described further on.

The dark brown alcoholic solution was digested for a long time with animal charcoal, filtered, and the bulk of the alcohol distilled off. On cooling, a beautifully crystalline body separated, which was purified by repeated recrystallisation.

The analysis gave numbers agreeing with the formula $(C_9H_6O_2)_n$.

I. 0.2343 gram substance gave 0.0941 gram H_2O and 0.6374 gram CO_2.

II. 0.1746 gram substance gave 0.0709 gram H_2O and 0.4722 gram CO_2.

	Found.		Theory,
	I.	II.	$(C_9H_6O_2)_n$.
C	74.19	73.76 per cent.	73.97 per cent.
H	4.41	4.51	4.11
O	21.40	21.73	21.92

This compound probably has the formula $C_{27}H_{18}O_6$, being formed from three molecules of ethylic benzoylacetate by the elimination of three molecules of alcohol, according to the equation—

$$3C_6H_5.CO.CH_2.COO.C_2H_5 = C_{27}H_{18}O_6 + 3C_2H_5.OH.$$

This substance melts at 273°–275°. It is sparingly soluble in cold alcohol, more easily in hot, and crystallises on cooling in beautiful silky plates, which strongly resemble anthracene, and give a beautiful play of colors with polarised light. It is almost insoluble in benzene, light petroleum and acetone. In ether and carbon bisulphide it is somewhat soluble, and on evaporation crystallises in glittering plates. The solution in carbon bisulphide is only very slowly acted on by bromine, hydrogen bromide being given off. On adding an ethereal solution of sodium ethoxide to the solution of the substance in warm ether, a voluminous precipitate of a sodium compound is thrown down; this is decomposed by treatment with acids with regeneration of the original compound.

This substance, however, is not a true acid. It dissolves easily in dilute alcoholic soda or sodium ethoxide, but is entirely reprecipitated on passing carbonic anhydride, so that in this case a sodium compound corresponding with that of ethylic benzoylacetate is formed, and not the sodium salt of an acid. If the solution in alcoholic potash is allowed to remain for some time, the compound is slowly but completely decomposed. On diluting the product with water, and acidifying with dilute sulphuric acid, an acid is precipitated which has all the properties of benzoylacetic acid. It melts at 80°–85°, gives the characteristic violet coloration with ferric chloride, and is decomposed into carbonic anhydride and acetophenone on heating. This acid appears to be produced almost quantitatively by the action of potash on the substance $C_{27}H_{18}O_6$.

If it is boiled with alcoholic potash, benzoic acid, acetophenone and other bodies are formed. Heated in a test-tube the compound $C_{27}H_{18}O_6$ sublimes partly unchanged, but most of it is decomposed, with separation of oily bodies, probably acetophenone. When distilled with zinc-dust a light boiling body is given off, which burns with a strongly luminous flame, and appears to be benzene. It is not decomposed by boiling with dilute sulphuric acid. It dissolves in concentrated sulphuric acid with a faint yellowish color, which is not perceptibly changed on warming. It is easily attacked by hot concentrated nitric acid, and on adding water to the product a yellowish mass is precipitated, which crystallises beautifully from alcohol, and is probably a nitro-derivative. On warming the compound $C_{27}H_{18}O_6$ with phenylhydrazine, it yields an intensely yellow body, which, however, was not further examined.

The yellow amorphous compound mentioned above (p. 106) as remaining when the compound $C_{27}H_{18}O_6$ was dissolved by treating the crude product with alcohol, was then further examined.

This substance melts above 300°. It is insoluble in most of the usual solvents, and can therefore be easily separated from impurities by repeated extraction with them. It is thus obtained as a light yellow amorphous mass, which gave the following numbers on analysis:

I. 0.1243 gram substance gave 0.0460 gram H_2O and 0.3380 gram CO_2.

II. 0.1556 gram substance gave 0.0586 gram H_2O and 0.4239 gram CO_2.

	Found.		Theory, $(C_9H_6O_2)_n$.
	I.	II.	
C	74.16 per cent.	74.29 per cent.	73.97 per cent.
H	4.11	4.18	4.11
O	21.73	21.53	21.92

The compound appears to be homogeneous, the above analyses having been made with two distinct preparations. It is possible that it may have the formula $C_{36}H_{24}O_8$, being a condensation-product of four molecules of ethylic benzoylacetate,

$$4C_6H_5.CO.CH_2.COO.C_2H_5 = C_{36}H_{24}O_8 + 4C_2H_5.OH.$$

It is an acid, and dissolves easily in sodium ethoxide, being reprecipitated by dilute sulphuric acid, but not by carbonic anhydride. It is also partially soluble in ammonia. On boiling it with sodium ethoxide a deep red solution is formed; this, when acidified, deposits a small quantity of an acid, the alcoholic solution of which gives a violet coloration with ferric chloride. The following is an extremely characteristic reaction of this substance. If the merest trace of it is mixed with concentrated sulphuric acid it dissolves to a yellowish solution, and on warming this the color changes slowly to a reddish-brown and then to a reddish-violet. If this solution be further heated a most intense bluish-violet coloration is produced, which becomes purple on strongly heating. The bluish-violet coloration is most beautiful, and strongly resembles methylene-blue. The color disappears on diluting with water.

Owing to the difficulty of obtaining any quantity of these last two condensation-products, I have not examined them further, but confined my attention to the dehydrobenzoylacetic acid.

Ethylic Dehydrobenzoylacetate.

In order to prepare this ethereal salt, silver dehydrobenzoylacetate was digested on a water-bath for two hours with excess of ethyl iodide and a little dry ether; in this way the salt was completely decomposed. After collecting and extracting the precipitated iodide of silver several times with ether, and evaporating the ethereal solution, a semi-solid mass was obtained, which was first spread on a porous plate to free the crystals from oily matter, and then several times recrystallised from benzene. When analysed it gave the following results:

0.1843 gram of substance gave 0.0858 gram H_2O and 0.5050 gram CO_2.

	Found.	Theory, $C_{17}H_{11}O_2.COOC_2H_5$.
C	74.73 per cent.	75.00 per cent.
H	5.17	5.20
O	20.00	20.00

This compound is therefore ethylic dehydrobenzoylacetate. It crystallises from benzene in almost colorless glittering needles which melt at 159°, and show a beautiful play of colors when examined with the polariscope. If carefully heated it appears to distil almost without decomposition.

It is moderately soluble in alcohol, acetone, benzene and bisulphide of carbon, more sparingly in ether and light petroleum. The solution in alcohol gives a reddish-brown coloration on the addition of a drop of ferric chloride. Warmed with alcoholic potash it is easily saponified, dehydrobenzoylacetic acid being generated.

Its alcoholic solution when mixed with phenylhydrazine yields an intensely yellow compound, which, however, has not yet been obtained pure enough for analysis; its formation is, however, a proof that the dehydrobenzoylacetic acid contains at least one carbonyl-group.

If an ethereal solution of ethylic dehydrobenzoylacetate is treated with an ethereal solution of sodic ethylate, an intensely yellow sodium compound is precipitated; but, unfortunately, ethylic dehydrobenzoylacetate is so sparingly soluble in ether that it was found impossible to obtain the compound in quantity sufficient for analysis.

In the course of some experiments on dehydracetic acid, the results of which I hope to make public at some future time, it was found that the methyl salt of this acid possesses the property of forming a sodium compound of the formula $C_8H_6O_4CH_3Na$, in which one hydrogen of the methyl compound is directly replaced by sodium.

It is extremely probable, therefore, that the sodium compound of ethylic dehydrobenzoylacetate is similarly constituted.

Action of Potassic Hydroxide on Dehydrobenzoylacetic Acid.

Dehydracetic acid is, as is well known, easily split up by heating with alkalis, into acetone, acetic acid and carbonic anhydride, according to the equation—

$$C_8H_8O_4 + 3H_2O = CH_3.CO.CH_3 + 2CH_3.COOH + CO_2.$$

It appeared likely, therefore, that by treating dehydrobenzoylacetic acid in the same way, similar decomposition-products would be produced, thus affording evidence that this acid and dehydracetic acid were analogous compounds.

In order to test this the action of potash on dehydrobenzoylacetic acid was carefully studied in the following way:

The pure acid was first dissolved in dilute alcoholic potash, and after an excess of a concentrated solution of the latter had been added, the whole was heated to boiling on a water-bath for several hours. During the reaction the mass became gradually darker; when finished, the smell of acetophenone was easily recognisable.

In order to isolate the products the alcohol was first slowly distilled off, water was then added, and the whole distilled in a current of steam. The distillate, which smelt strongly of acetophenone, contained small particles of oil, which were separated from the watery liquid by shaking with ether. On evaporating the ether a colorless oil remained, which, on fractioning, went over entirely between 195°–200°, and was undoubtedly acetophenone. This was confirmed by shaking it with a solution of orthonitrobenzaldehyde in dilute soda; in a short time an indigo-blue precipitate separated in considerable quantity.

The alkaline solution which was freed from the acetophenone in the way above described was acidified with dilute sulphuric acid, and again distilled, when an acid liquid passed over which smelt distinctly of acetic acid; the quantity, however, was so small that an analysis could not be performed. The residue in the retort was then several times extracted with ether, and on evaporating the solution, a dark-brown semi-solid acid was obtained. This was first separated from oily matter by spreading it out on a porous plate, and then recrystallised from water. In this way it was obtained in colorless needles melting at 118°–120°, and possessing all the properties of benzoic acid, with which it was undoubtedly identical.

Dehydrobenzoylacetic acid is therefore decomposed on heating with alcoholic potash into acetophenone, acetic acid, benzoic acid and carbonic anhydride, according to the equation—

$$C_{18}H_{12}O_4 + 3H_2O = C_6H_5.CO.CH_3 + CH_3.COOH + C_6H_5.COOH + CO_2.$$

The reaction is perfectly analogous to the formation of two molecules of acetic acid and one of acetone by the action of potash on dehydracetic acid.

In the course of these experiments it was noticed that when the boiling with potash was continued for a short time only, the benzoic acid obtained was always mixed with a certain quantity of another acid, the alcoholic solution of which gave a violet coloration with ferric chloride, strongly resembling that produced by benzoylacetic acid. In order, if possible, to obtain this acid in larger quantity, the action of potash on dehydrobenzoylacetic acid was tried in the cold, and it was found that it was completely decomposed if mixed with a concentrated solution of alcoholic potash and allowed to remain for twelve hours. The mass became dark reddish-brown, and in a short time a considerable quantity of a potash salt crystallised out in glittering plates. On adding water the whole dissolved, forming a reddish-brown solution, which smelt only very faintly of acetophenone. In order to isolate the products of the reaction the alkaline liquid was well cooled, acidified with dilute sulphuric acid, and once or twice extracted with ether. On allowing the ethereal solution to evaporate a quantity of a dark brownish acid was left, which was purified from oily matter by spreading it out on a porous plate, and thus obtained as a slightly yellowish, hard, crystalline mass. This was dissolved in dilute ammonia, well shaken with pure animal charcoal, and filtered. In this way an almost colorless solution of the ammonium salt was obtained, which was acidified with dilute sulphuric acid and extracted with ether. The ethereal solution, on evaporation, deposited a faintly yellowish-colored crystalline acid; this, after drying over sulphuric acid in a vacuum, gave the following numbers on analysis:

0.1796 gram of substance gave 0.0841 gram H_2O and 0.432 gram CO_2.

	Found.	Theory, $C_9H_8O_3$.
C	65.62 per cent.	65.85 per cent.
H	5.23	4.88
O	29.15	29.27

This acid has, therefore, the same constitution as benzoylacetic acid, and is undoubtedly identical with it. It melted at 83°–85° (after recrystallising from benzene at 98°–100°), and exhibited all the properties of benzoylacetic acid. The solution in alcohol gives an intense violet coloration with ferric chloride, and the free acid, when distilled, is split up into acetophenone and carbonic anhydride. In order to be certain that the acid obtained from the dehydrobenzoylacetic acid really had the constitution $C_9H_8O_3$, it was converted into the silver salt, and analysed with the following result:

0.1463 gram substance gave 0.0592 gram silver.

	Found.	Theory, $C_6H_5.CO.CH_2.COOAg$.
Ag	40.36 per cent.	39.84 per cent.

There is therefore no doubt that dehydrobenzoylacetic acid, when treated with alcoholic potash in the cold, is converted into benzoylacetic acid, according to the equation—

$$C_{18}H_{12}O_4 + 2H_2O = 2C_6H_5.CO.CH_2.COOH.$$

This reaction is exactly the reverse of its formation from two molecules of ethylic benzoylacetate.

In order to determine whether this decomposition really did take place according to the above reaction, some quantitative experiments were made, and the amount of benzoylacetic acid produced weighed. 3 grams of pure dehydrobenzoylacetic acid were mixed with a concentrated solution of alcoholic potash, and allowed to stand at the ordinary temperature until a very faint smell of acetophenone was perceptible. The product was then treated as described above. After evaporating the ethereal extract of the acid formed in a weighed dish, 3.15 grams of crude product were obtained (calculated for the above equation 3.3 grams). After spreading it out on a porous plate, and thus removing a trace of oily matter, the almost colorless acid left weighed nearly 3 grams. It was then treated with ammonia and animal charcoal, and gave 2.8 grams of nearly pure benzoylacetic acid.

In order to be sure that this acid was benzoylacetic acid it was heated in a retort until the whole was decomposed, and the resulting oil dissolved in ether and shaken with a dilute solution of sodic hydroxide. On acidifying the alkaline solution and extracting with ether, a very small quantity of benzoic acid was obtained. The neutral oil formed by the decomposition showed the boiling-point of 195°, and was undoubtedly acetophenone. It is probable, therefore, that on boiling dehydrobenzoylacetic acid with potash benzoylacetic acid is first formed, which is then further decomposed into benzoic acid, acetic acid, acetophenone and carbonic anhydride.

Reduction of Dehydrobenzoylacetic Acid.

Dehydrobenzoylacetic acid, $C_{18}H_{12}O_4$, besides the carboxyl-group, contains two atoms of hydrogen, one of which at least must be present in the ketone form, CO, from the fact that the acid combines with phenylhydrazine. This phenylhydrazine compound could be obtained crystalline only with difficulty, and then in such small quantity that a complete analysis could not be made, but only a nitrogen determination, which seemed to show that the body had the formula $C_{18}H_{12}O_3.N_2H.C_6H_5$, one molecule of the acid combining with one molecule of phenylhydrazine. In order to obtain some idea as to the condition of the fourth oxygen-atom in the molecule $C_{18}H_{12}O_4$, it was next treated with reducing agents under different conditions, the best results being obtained with sodium amalgam in the following way :

Dehydrobenzoylacetic acid was dissolved in dilute sodic hydroxide and an excess of liquid sodium amalgam slowly added, the whole being well cooled during the operation, and the product allowed to stand for twenty-four hours in order to ensure complete reduction.

At first no evolution of hydrogen was perceptible, but towards the end of the reaction a quantity of gas was given off and a small amount of a resinous body formed, which was filtered off from the alkaline solution, but was too small for further examination. On acidifying the filtrate with dilute sulphuric acid it deposited an almost colorless amorphous acid, which was collected, well washed with water and spread out on a porous plate to free it from traces of oily matter. This crude product was dissolved in a little boiling benzene and then light petroleum boiling at 70°–80° added until a slight turbidity was produced. On standing, this solution deposited a quantity of a new acid in colorless plates, which were obtained pure by recrystallisation from benzene and light petroleum.

The analysis gave the following numbers:

I. 0.1665 gram substance gave 0.0761 gram H_2O and 0.4750 gram CO_2.

II. 0.1485 gram substance gave 0.0669 gram H_2O and 0.4247 gram CO_2.

III. 0.1782 gram substance gave 0.0723 gram H_2O and 0.5097 gram CO_2.

	Found.			Theory, $C_{18}H_{12}O_3$.
	I.	II.	III.	
C	77.81	77.99	78.09 per cent.	78.26 per cent.
H	5.07	5.00	4.51	4.35
O	17.12	17.01	17.40	17.39

This acid, therefore, has the formula $C_{18}H_{12}O_3$, and is produced from dehydrobenzoylacetic acid by the addition of two atoms of hydrogen and the elimination of the elements of water according to the equation—

$$C_{18}H_{12}O_4 + H_2 = C_{18}H_{12}O_3 + H_2O.$$

The yield of this acid is very small, and it appears to be formed only under certain conditions, the principal product of the reaction being the acid $C_{18}H_{14}O_4$, which will be described later on. In this reduction by far the greater part of the dehydrobenzoylacetic acid is entirely decomposed, a quantity of oily and resinous products being formed, which render the purification of the acids very difficult. It is curious that a considerable quantity of benzaldehyde always appears to be formed during the reduction. The acid $C_{18}H_{12}O_3$ melts at 112°. It is easily soluble in alcohol, benzene, ether, chloroform and bisulphide of carbon, almost insoluble in light petroleum. It is difficult to obtain it well crystallised, a mixture of benzene and light petroleum being the best solvents to crystallise it from. The bisulphide of carbon solution does not decolorise bromine.

The acid dissolves in concentrated sulphuric acid with an intense orange coloration, which, on warming, first disappears and then turns to a greenish-brown.

Apparently, it is a very stable body, and is not affected by potassium permanganate in the cold, and only slowly on warming. Heated by itself in a test-tube it is decomposed into carbonic anhydride and high-boiling oils, a considerable quantity of carbonaceous matter being left behind. No acetophenone is formed when it is distilled with soda-lime.

The acid dissolves in soda and ammonia slowly in the cold, more rapidly on heating. The sodium salt is best prepared by dissolving the acid in a little alcohol, neutralising with soda, and allowing the solution to evaporate over sulphuric acid in a vacuum. Thus obtained it is an almost colorless syrup easily soluble in water; the solution, exposed for a long time over sulphuric acid in a vacuum, slowly deposits crystals. The quantity of this acid, $C_{18}H_{12}O_3$, which I obtained was unfortunately insufficient to allow of the further examination and analysis of its salts. The products of the reduction of dehydracetic acid were first examined by Oppenheim and Precht,[1] who, by treating this body with zinc and hydrochloric acid, obtained an acid melting at 187°; this, however, they did not further examine, only stating that it was not a simple reduction-product, but that it appeared to contain less oxygen than the dehydracetic acid. Schibbye,[2] who, during some experiments on dehydracetic acid, repeated this reaction, and analysed the acid and its barium salt, gave to the former the formula $C_8H_{10}O_3$, it being formed from dehydracetic acid according to the equation—

$$C_8H_8O_4 + 2H_2 = C_8H_{10}O_3 + H_2O.$$

If the reaction takes place in this way it is possible that the acid $C_{18}H_{12}O_3$, described above, is constituted similarly to the acid $C_8H_{10}O_3$, in which case the constitution of the former would have to be changed to $C_{18}H_{14}O_3$. I am at present engaged in some experiments to decide this point.

In order to isolate any other products of the reaction of dehydrobenzoylacetic acid, the mother-liquors from the acid $C_{18}H_{12}O_3$ were next evaporated to dryness, the semi-solid residue dissolved in a little alcohol, and light petroleum boiling at 70°–80° added until the liquid became slightly turbid. On allowing the solution to evaporate at the ordinary temperature, a new acid crystallised out in small needles, which were collected, washed with alcohol and light petroleum, and dried at 110°. The analysis gave the following results:

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[1] Berichte **9**, 1101.

[2] Inaugural Dissertation, Würzburg, 1882.

I. 0.1568 gram substance gave 0.0731 gram H_2O and 0.4239 gram CO_2.

II. 0.1614 gram substance gave 0.0758 gram H_2O and 0.4364 gram CO_2.

III. 0.1511 gram substance gave 0.0705 gram H_2O and 0.4064 gram CO_2.

	Found.			Theory, $C_{18}H_{14}O_4$.
	I.	II.	III.	
C	73·73	73·74	73·36 per cent.	73·47 per cent.
H	5.18	5.22	5.18	4·76
O	21.09	21.04	21.46	21.76

The acid, therefore, has the formula $C_{18}H_{14}O_4$, and is formed from dehydrobenzoylacetic acid by the addition of two atoms of hydrogen, according to the equation—

$$C_{18}H_{12}O_4 + H_2 = C_{18}H_{14}O_4.$$

It crystallises from a mixture of alcohol and light petroleum in small yellow needles which melt at 145°–150° with decomposition and evolution of carbonic anhydride. It is easily soluble in most of the usual solvents, but only sparingly in light petroleum and cold bisulphide of carbon. From its hot solution in the latter it is deposited on cooling in nodules, seldom in well-formed crystals. The solution in bisulphide of carbon does not decolorise bromine at ordinary temperatures, but on warming hydrogen bromide is given off, and a brominated acid formed which crystallises out in small needles on cooling.

The acid $C_{18}H_{14}O_4$ is moderately soluble in dilute alkalis, especially on warming, and is reprecipitated on the addition of an acid. It dissolves in concentrated sulphuric acid, forming a yellow solution, which changes to brownish-red on warming. When heated in a test-tube it melts and gives off carbonic anhydride, a low-boiling oil distilling over with an odor like benzene; if the heating be continued the greater part chars, a small quantity of a heavy oil being formed which becomes solid on cooling, and appears to be benzoic acid. On distilling the acid with soda-lime a small amount of an oil of low boiling-point is formed, but no acetophenone.

Action of Acetic Anhydride on the Acid $C_{18}H_{14}O_4$.

From the formula of this acid it would seem to be the intermediate product in the formation of the acid $C_{18}H_{12}O_3$ by the reduction of dehydrobenzoylacetic acid, thus:

$$C_{18}H_{12}O_4 + H_2 = C_{18}H_{14}O_4 = C_{18}H_{12}O_3 + H_2O.$$

It appeared probable, therefore, that by treating it with some dehydrating agent, such as acetic anhydride, the acid $C_{18}H_{12}O_3$ would be produced. In order to test this two grams of the acid $C_{18}H_{14}O_4$ were heated with an excess of acetic anhydride in a flask connected with a reflux condenser for about one hour. Water was then added, and the precipitated product after washing with water was crystallised from 80 per cent. acetic acid. The analysis gave the following result:

I. 0.1910 gram substance gave 0.0817 gram H_3O and 0.5292 gram CO_2.

II. 0.2124 gram substance gave 0.0908 gram H_2O and 0.5871 gram CO_2.

	Found.		Theory,
	I.	II.	$C_{20}H_{14}O_4$.
C	75.57	75.39 per cent.	75.47 per cent.
H	4.75	4.75	4.40
O	19.68	19.86	20.13

This compound appears, therefore, to have the formula $C_{20}H_{14}O_4$, and it would seem as if the acetic anhydride had not only acted as a dehydrating agent, but that an acetate had also been formed, according to the equation—

$$C_{18}H_{14}O_4 + 2\begin{matrix}CH_3.CO\\CH_3.CO\end{matrix}\!>\!O = C_{20}H_{14}O_4 + 3CH_3.COOH.$$

It is, however, impossible to come to any definite conclusion from this result, as the amount of material at my disposal was so small that I was unable to try this reaction again, and confirm the constitution of the compound $C_{20}H_{14}O_4$ by further analyses. It crystallises from acetic acid in yellow needles which melt at 145°–150°. Heated in a test-tube it first melts, and then gives off carbonic anhydride and acetic anhydride. From the ease with which it gives up its acetic anhydride it is possible that it is nothing more than a mixed anhydride of the acid $C_{18}H_{12}O_3$ and acetic acid. It is easily soluble in hot alcohol, less so in cold. It dissolves easily in benzene and chloroform, but only sparingly in ether and bisulphide of carbon: in light petroleum it is almost insoluble. It is precipitated in small needles from its solution in benzene on adding light petroleum, and can be purified in this manner. It crystallises, however, best from dilute acetic acid (80 per cent.).

The alcoholic solution gives an intense scarlet coloration with ferric chloride. The compound is moderately soluble in ammonia, sodium hydroxide and carbonate, especially on warming. It dissolves in concentrated sulphuric acid, forming an orange solution, which changes to brown on heating. This coloration does not disappear on diluting with water.

Heated with alcoholic potash it is easily saponified, acetic acid and another acid being formed.

Action of Phosphorous Pentachloride on Dehydrobenzoylacetic Acid.

In order, if possible, to obtain some further clue as to the constitution of dehydrobenzoylacetic acid, it was next treated with phosphorous pentachloride. By this means, not only the carboxyl-group, but also any carbonyl- or hydroxyl-groups would be acted on and be replaced by chlorine, whereas any oxygen present in the indifferent or oxide form would remain intact, and could be easily recognised.

If dehydrobenzoylacetic acid is mixed with phosphorous pentachloride a very energetic reaction sets in, the whole becoming very hot and most of the acid being charred, so that it was found impossible to extract any crystalline compound from the product. It was necessary, therefore, to moderate the violence of the reaction by diluting with oxychloride of phosphorus and cooling, the experiment being carried out in the following way:

5 grams of dehydrobenzoylacetic acid were mixed with 30 grams of phosphorous oxychloride, and then 10 grams of phosphorous pentachloride were slowly added, the whole being kept thoroughly cooled with ice-water. The acid slowly dissolved in the mixture, forming a yellowish-brown solution, and on standing a quantity of yellow crystals were deposited, which, however, at a later stage of the reaction, disappeared again almost entirely. After remaining for twelve hours the product was poured into ice-water, when a yellowish semi-solid mass was precipitated; this was collected, well

washed with water, and dried over sulphuric acid in a vacuum. In about forty-eight hours the mass, which had become hard and brittle, was powdered and extracted with small quantities of hot alcohol, in which it was sparingly soluble, and filtered. The filtrate on cooling deposited a yellowish crystalline substance, which by one or two recrystallisations from methyl alcohol was obtained pure in colorless plates melting at 227°–229°.

The amount of this compound obtained by the above reaction was, however, so small that no analysis could be made. It appeared to contain only traces of chlorine. It is colored yellow on being warmed with potash.

The residue left after extracting the above-described substance with alcohol was dissolved in boiling methyl alcohol, from which it was deposited on cooling in beautiful brownish-colored glittering plates. On repeated recrystallisation from the same solvent it was easily obtained pure. For the analysis it was dried at 120° and then gave the following results:

I. 0.2114 gram substance gave 0.0691 gram H_2O and 0.5370 gram CO_2.

II. 0.2226 gram substance gave 0.0758 gram H_2O and 0.5668 gram CO_2.

III. 0.1394 gram substance gave 0.0665 gram AgCl.

IV. 0.2363 gram substance gave 0.1110 gram AgCl.

V. 0.2415 gram substance gave 0.1128 gram AgCl.

	Found.					Theory,
	I.	II.	III.	IV.	V.	$C_{18}H_{11}O_3Cl$.
C	69.28	69.44	...	...	...	69.56 per cent.
H	3.63	3.78	...	...	...	3.55
Cl	...	...	11.80	11.63	11.58	11.43

The compound, therefore, has the formula $C_{18}H_{11}O_3Cl$. When crystallised from methyl alcohol it forms brownish-colored plates melting at 150°–151°.

It is sparingly soluble in ether, alcohol, benzene and light petroleum, more easily in hot methyl alcohol and acetic acid. The hot alcoholic solution gives a reddish-brown coloration with ferric chloride. It dissolves with difficulty in sodium hydroxide, ammonia and sodium carbonate, forming yellow solutions, which, when acidified, deposit a colorless amorphous acid. On boiling with alcoholic potash for a short time, however, it is easily decomposed, and on evaporating the alcohol and adding water, a dark brownish solution of a potassium salt is obtained; this, when acidified, deposits an oily acid, which was extracted with ether. On allowing the ethereal solution to evaporate a thick oily acid was obtained, and on standing a small quantity of a crystalline body was deposited; this, however, could not be obtained pure enough for analysis. The alcoholic solution of this acid gives an intense violet coloration with ferric chloride, very similar to that produced by benzoylacetic acid. As the formation of this latter acid appeared possible, the crude product of the above reaction was distilled, and a few drops of a brownish oil obtained, which smelt decidedly of acetophenone. The quantity was too small, however, to determine the boiling-point, and I was therefore unfortunately unable to decide definitely whether benzoylacetic acid had been formed or not. It appears, however, to be extremely probable. On simply warming the compound $C_{18}H_{11}O_3Cl$ with alcoholic potash it dissolves completely, and after a short time a potash salt crystallises out; this, when acidified, yields an acid which also gives the violet coloration with ferric chloride. On prolonged boiling with alcoholic potash, however, a neutral body is formed, and only a trace of the above acid. If a solution of this chloride in ether is treated with an ethereal solution of sodium ethoxide, a beautiful yellow sodium compound is precipitated. From these experiments it would seem that the compound $C_{18}H_{11}O_3Cl$ is in reality a chlorinated acid of the formula $C_{17}H_{10}OCl.COOH$, and not the acid chloride $C_{17}H_{11}O_2.COCl$, as might be expected from the mode of formation. In the latter case we should expect that dehydrobenzoylacetic acid would be regenerated on treating it with water; or on treating it with boiling alcohol or sodium ethoxide, that the ethylic salt of the latter would be formed, reactions which as a fact do not take place. I therefore propose to name the compound $C_{18}H_{11}O_3Cl$, "Chlorodehydrobenzoylacetic acid."

Heated by itself in small quantities at a time it first melts, and then at a high temperature a thick brown oil distils over, which on cooling slowly solidifies, a small quantity of a carbonaceous residue being left. The distillate after washing with a little alcohol melts at 147°–149°, and appears to be the unchanged substance, a proof that it is very stable. Chlorodehydrobenzoylacetic acid is easily reduced by warming it with zinc-dust and acetic acid. On adding water a pale yellowish substance is obtained, which is free from chlorine. After collecting and washing with water the residue was dissolved in a little hot alcohol, from which it separated on cooling in amorphous flakes. On heating, this substance becomes brownish at about 130°, and melts at between 155°–160°; at a higher temperature carbonic anhydride is given off, and a blackish tarry residue is left. It dissolves in concentrated sulphuric acid with a beautiful purple color, but the solution soon becomes discolored on standing. It dissolves easily in benzene, and is precipitated in yellowish flakes on adding light petroleum, but as it could not be obtained in crystalline form from these or any other solvents, it was not analysed.

By the action of phosphorous pentachloride on dehydracetic acid, Oppenheim and Precht[1] obtained a compound of the formula $C_8H_6O_2Cl_2$, which is possibly the product of the further action of the above reagent on an unstable body $C_8H_7O_3Cl$, the latter being similarly constituted to chlorodehydrobenzoylacetic acid. In order to test this the action of an excess of phosphorous pentachloride on the compound $C_{18}H_{11}O_3Cl$ was tried, and, as a fact, traces of a second body were obtained, which, however, owing to the small quantity of material at my disposal, could not be further examined.

Constitution of Dehydrobenzoylacetic Acid.

Dehydrobenzoylacetic acid, $C_{18}H_{12}O_4$, contains besides a carboxyl-group COOH, and a carbonyl-group CO, a fourth atom of oxygen, which, on account of its indifference towards acetic anhydride, reducing agents and phosphorous pentachloride, can neither be present in the ketone form (CO) nor as hydroxyl, OH, and must therefore be in the ether form—*i. e.*, joined with its two affinities to two different carbon-atoms, thus: $\vdots$C.O.C$\vdots$. It is clear, moreover, that this acid contains two phenyl-groups, otherwise it could not be split up into two molecules of benzoylacetic acid on treatment with alcoholic potash.

In endeavoring from these facts to establish a formula for dehydrobenzoylacetic acid, it is first important to bear in mind that it is evidently formed by the elimination of two molecules of water from two molecules of benzoylacetic acid, thus:

$$\begin{matrix} C_6H_5.CO.CH_2.COOH \\ C_6H_5.CO.CH_2.COOH \end{matrix} = C_{18}H_{12}O_4 + 2H_2O.$$

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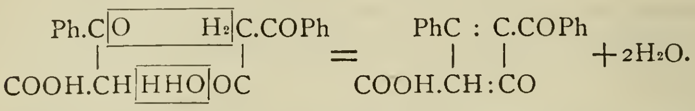
[1] Berichte 9, 1100.

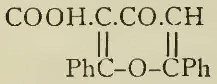
Dehydrobenzoylacetic acid is, however, a monobasic acid, forming salts of the formula $C_{18}H_{11}O_4M$, so that it follows that the carboxyl-group of one of the molecules of benzoylacetic acid must condense in some way with the second molecule of the latter, one molecule of water being eliminated. This intermediate product then loses a second molecule of water, dehydrobenzoylacetic acid being formed. The simplest way in which this condensation of two molecules of benzoylacetic acid can take place is the following:



$$\begin{array}{l} \text{Ph.C}\boxed{\text{O}\qquad\text{H}_2}\text{C.COPh} \\ \quad | \qquad\qquad\quad | \\ \text{COOH.CH}\boxed{\text{HHO}}\text{OC} \end{array} = \begin{array}{l} \quad\text{PhC : C.COPh} \\ \qquad | \quad\; | \\ \text{COOH.CH:CO} \end{array} + 2H_2O.$$

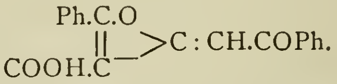
That this formula is not the right one is evident, as it not only contains two ketone-groups, but is so strongly bound together that the splitting up into two molecules of benzoylacetic acid, on simply standing in contact with potash, would be extremely difficult to account for. Besides the above there are two other possible formulæ for dehydrobenzoylacetic acid, which can be built up on the assumption that the carboxyl-group of one molecule of benzoylacetic acid takes part in the reaction—namely:

I.



$$\begin{array}{l} \text{COOH.C.CO.CH} \\ \qquad\;\; \| \quad\;\; \| \\ \quad\;\, \text{PhC–O–CPh} \end{array}$$

II.

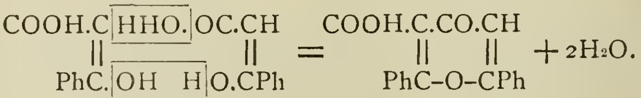


$$\begin{array}{l} \qquad\quad \text{Ph.C.O} \\ \qquad\qquad \| \\ \text{COOH.C} \end{array} \!\!>\text{C : CH.COPh.}$$

In the formation of these two formulæ it is necessary to suppose that, as in almost all condensations of ethylic benzoylacetate and acetoacetate, the molecule first undergoes an internal change, thus

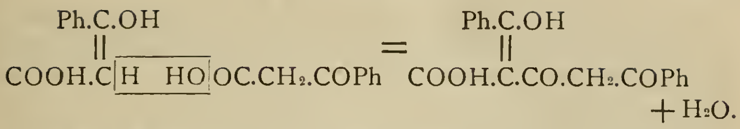
$$\underset{\text{Stable form.}}{C_6H_5.CO.CH_2.COOH} = \underset{\text{Mobile form.}}{C_6H_5.C(OH):CH.COOH.}$$

In formula I the condensation takes place between two such mobile forms, thus:



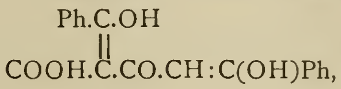
$$\begin{array}{l} \text{COOH.C}\boxed{\text{HHO.}}\text{OC.CH} \\ \qquad\quad \| \qquad\qquad\quad \| \\ \quad\;\, \text{PhC.}\boxed{\text{OH}\quad\text{H}}\text{O.CPh} \end{array} = \begin{array}{l} \text{COOH.C.CO.CH} \\ \qquad\;\; \| \quad\;\; \| \\ \quad\;\, \text{PhC–O–CPh} \end{array} + 2H_2O.$$

Formula II is formed in two stages. In the first place the carboxyl-group of one molecule of benzoylacetic acid (in the stable form) condenses with the second molecule (in the mobile form) in the following way:



$$\begin{array}{l}\text{Ph.C.OH}\\ \quad\;\|\\ \text{COOH.C}\boxed{\text{H HO}}\text{OC.CH}_2\text{.COPh}\end{array} = \begin{array}{l}\text{Ph.C.OH}\\ \quad\;\|\\ \text{COOH.C.CO.CH}_2\text{.COPh}\end{array} + \text{H}_2\text{O}.$$

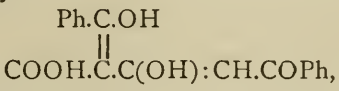
In the second part of the condensation this intermediate body must be transformed into the mobile form, which can take place in two ways. In the first place one of the hydrogen-atoms of the CH_2-group can react with the CO-group next to the phenyl-group, when the following mobile intermediate body would be formed:



$$\begin{array}{l}\qquad\;\text{Ph.C.OH}\\ \qquad\qquad\|\\ \text{COOH.C.CO.CH:C(OH)Ph,}\end{array}$$

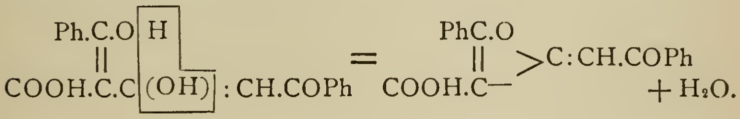
which, on removing the elements of water from the two hydroxyl-groups, gives formula I.

In the second place the molecular change can take place between the CH_2-group and the other ketone-group, and thus give the following body:



$$\begin{array}{l}\qquad\;\text{Ph.C.OH}\\ \qquad\qquad\|\\ \text{COOH.C.C(OH):CH.COPh,}\end{array}$$

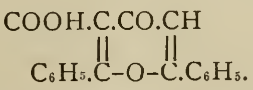
which, on the elimination of water, gives formula II, thus:



$$\begin{array}{l}\;\;\text{Ph.C.O}\boxed{\text{H}}\\ \qquad\;\|\\ \text{COOH.C.C}\boxed{\text{(OH)}}\text{:CH.COPh}\end{array} = \begin{array}{l}\text{PhC.O}\\ \quad\;\| \;\;>\text{C:CH.COPh}\\ \text{COOH.C}-\end{array} + \text{H}_2\text{O}.$$

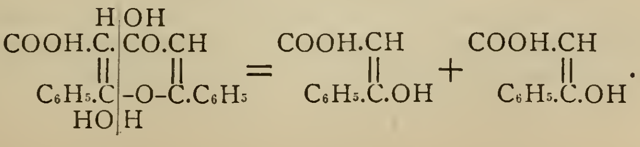
Of these two formulæ it is evident that, apart from the complicated formation of formula II, formula I is the most likely, as it explains best of all the reactions in which the acid takes part.

I therefore suggest as the most probable constitution of the dehydrobenzoylacetic acid the following formula:



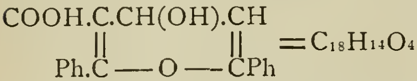
$$\begin{array}{l}\text{COOH.C.CO.CH}\\ \qquad\;\;\|\qquad\;\|\\ \;\;\text{C}_6\text{H}_5\text{.C–O–C.C}_6\text{H}_5.\end{array}$$

This body is split up on treatment with alcoholic potash into two molecules of benzoylacetic acid, thus:

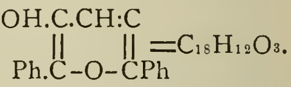


$$\begin{array}{l}\qquad\quad\;\;\text{H}\,|\,\text{OH}\\ \text{COOH.C.}\,|\,\text{CO.CH}\\ \qquad\quad\;\|\;|\quad\;\;\|\\ \;\;\text{C}_6\text{H}_5\text{.C}\,|\,\text{–O–C.C}_6\text{H}_5\\ \qquad\quad\;\text{HO}\,|\,\text{H}\end{array} = \begin{array}{l}\;\;\text{COOH.CH}\\ \qquad\quad\;\|\\ \text{C}_6\text{H}_5\text{.C.OH}\end{array} + \begin{array}{l}\;\;\text{COOH.CH}\\ \qquad\quad\;\|\\ \text{C}_6\text{H}_5\text{.C.OH}\end{array}.$$

The two acids, $C_{18}H_{14}O_4$ and $C_{18}H_{12}O_3$, produced by the action of nascent hydrogen on dehydrobenzoylacetic acid would therefore have the following formulæ :



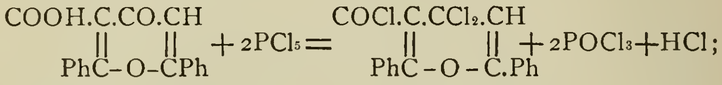
$$\begin{array}{l}\text{COOH.C.CH(OH).CH}\\ \qquad\ \|\qquad\qquad\quad \|\\ \quad\text{Ph.C — O — CPh}\end{array} = C_{18}H_{14}O_4$$



$$\begin{array}{l}\text{COOH.C.CH:C}\\ \qquad\ \|\qquad\ \|\\ \text{Ph.C-O-CPh}\end{array} = C_{18}H_{12}O_3.$$

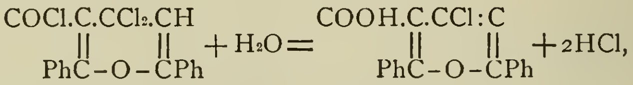
The formation of chlorodehydrobenzoylacetic acid by the action of pentachloride of phosphorus on dehydrobenzoylacetic acid undoubtedly takes place in two stages :

I.



$$\begin{array}{l}\text{COOH.C.CO.CH}\\ \qquad\ \|\qquad \|\\ \quad\text{PhC-O-CPh}\end{array} + 2PCl_5 = \begin{array}{l}\text{COCl.C.CCl}_2\text{.CH}\\ \qquad\ \|\qquad\quad \|\\ \quad\text{PhC-O-C.Ph}\end{array} + 2POCl_3 + HCl;$$

II.



$$\begin{array}{l}\text{COCl.C.CCl}_2\text{.CH}\\ \qquad\ \|\qquad\quad \|\\ \quad\text{PhC-O-CPh}\end{array} + H_2O = \begin{array}{l}\text{COOH.C.CCl:C}\\ \qquad\ \|\qquad \|\\ \quad\text{PhC-O-CPh}\end{array} + 2HCl,$$

this reaction being in every way analogous to the formation of chlorocinnamic acid by the action of pentachloride of phosphorus on ethylic benzoylacetate as described in Part II[1] of this research.

On comparing the properties of dehydrobenzoylacetic acid with those of the dehydracetic acid it is evident that, although some minor differences do exist, these two compounds are most probably of an analogous constitution; and as the former is extremely difficult to get in any quantity, I have commenced working on the latter, and hope at some future time to make public the results of my experiments.

ON A SOURCE OF ERROR IN THE ESTIMATION OF UREA BY THE HYPOBROMITE METHOD, WITH APPARATUS OF THE RUSSELL AND WEST TYPE.

By Walter D. Green.

Of the many forms of apparatus employed for estimating the amount of urea contained in urine by means of akaline hypobromite or hypochlorite solutions, probably the one most used by physicians is that devised by Russell and West. These experimenters, by using an alkaline solution of sodium hypobromite, and measuring the nitrogen evolved from the decomposition of the urea in urine, found that with their apparatus 94 or 95 per cent. of the urea present could be estimated. The reaction may be expressed as follows:

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[1] This Journal **7**, 153.

$$(NH_2)_2CO + 3NaBrO = 2H_2O + CO_2 + 3NaBr + N_2.$$

According to Knop,[1] the solution of sodium hypobromite should be prepared as follows: Dissolve 100 grams of sodium hydroxide in 250 cc. of water. Allow this solution to cool, and then add 25 cc. of bromine. Upon cooling, the reagent is ready for use. Thus prepared, the solution contains 62.5 grams free sodium hydroxide. Hitherto it has been thought that all the carbon dioxide evolved during the decomposition of the urea was absorbed by the free sodium hydroxide in the hypobromite solution to form sodium carbonate, and in employing this method with the Russell and West apparatus, the percentage of urea has been found to be equal to that originally present in the urea solution employed, and sometimes rather in excess of the amount really present. This was suspected to be due to the non-absorption of an appreciable quantity of the carbon dioxide evolved during the decomposition of the urea. In order to determine this, the following described apparatus was devised and the accompanying experiments performed: the object being to ascertain if any carbon dioxide was collected unabsorbed with the nitrogen and was measured as nitrogen, and if so, to what extent this took place. The apparatus consisted of a wide-necked bottle containing a small test-tube, in which the decomposition of the urea was to take place, closely stoppered with a rubber cork through which two glass tubes pass, one of which can be pushed down to within an inch of the bottom of the bottle. Connected with this tube upon one side of the bottle was a drying apparatus, consisting of five cylinders, containing respectively a solution of calcium hydrate, caustic soda in sticks, barium hydrate solution, and caustic soda in sticks. The air being admitted to the first cylinder, passes successively through them and is deprived of its carbon dioxide. A pinch-cock prevents any gas during its evolution in the bottle from passing into the cylinders. Attached to the remaining tube emerging from the bottle was a drying-tube containing calcium chloride in small pieces. Next were the Geissler's bulbs for collecting the carbon dioxide escaping absorption in the bottle. These were followed by another calcium chloride drying-tube to prevent access of any moisture from the atmosphere. A rubber tube attached to this drying-tube and connected with an aspirator, rendered it possible to exhaust the apparatus.

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[1] Chem. Centralbl. 1860, 244.

To detect qualitatively the presence of carbon dioxide with the nitrogen, a U-tube containing a strong solution of barium hydrate was inserted in place of the Geissler's bulbs. The urea solution was placed in a small test-tube, and introduced into the bottle into which 30 cc. of the hypobromite solution had been poured, and the pinch-cock between it and the drying-cylinders closed. Then upon inclining the bottle containing the reagent with the urea solution in the test-tube, immediate decomposition ensued with the evolution of gas. Ten minutes after the completion of the decomposition in the bottle, the first described tube passing through the cork was pushed down to within half an inch of the surface of the liquid in the bottle, and the pinch-cocks having been opened, aspiration was begun, and air free from carbon dioxide was slowly drawn through the apparatus for about half an hour.

The presence of carbon dioxide was demonstrated several times without doubt by the turbidity of the barium hydrate solution in the U-tube, upon drawing pure air through the bottle in which the decomposition occurred. To determine the actual amount of carbon dioxide passing over with the nitrogen, a weighed set of Geissler's bulbs, containing a strong solution of potassium hydrate, was placed in the position previously occupied by the U-tube after the calcium chloride tube, and connected as before. The method of procedure as to aspiration, etc., was the same as previously described. The bulbs were weighed both before each experiment and at its close, being at these times and as soon as detached from the apparatus tightly corked with rubber, so as to exclude admission of carbon dioxide and moisture from the air. The increase in weight after the passage of the gas is equal to the amount of carbon dioxide absorbed, which in the use of the Russell and West apparatus and of apparatus of that general design is measured as nitrogen. The accompanying table shows the results of fourteen quantitative experiments made with varying quantities of a 5 per cent. urea solution:

No. of Experiment.	No. cc. urea used.	Increase in weight of Geissler bulbs.	Equivalent volume of CO_2 in cc.
1	1	0.001	0.508
2	1	0.0003	0.152
3	1	0.0003	0.152
4	1	0.0007	0.355
5	2	0.001	0.507
6	1	0.0002	0.1015
7	2	0.0011	0.558
8	2	0.0017	0.862
9	2	0.0007	0.355
10	3	0.0004	0.202
11	3	0.0026	1.318
12	3	0.0011	0.558
13	4	0.0012	0.608
14	4	0.0049	2.485

Upon examination of the foregoing results it will be observed that an appreciable quantity of carbon dioxide escapes absorption by the free sodium hydrate contained in the sodium hypobromite solution, and passing out along with the nitrogen, is measured as such, thus increasing the apparent amount of urea in the solution undergoing analysis. The objection to the employment of the Russell and West type of apparatus is this non-absorption of all the carbon dioxide, which is most likely due to the immediate decomposition of the urea coming into contact with *only the surface* of the hypobromite solution in the bottle. This decomposition takes place so rapidly that sufficient time is not allowed for absorption of the carbon dioxide by the caustic soda, and possibly too the caustic soda in the immediate vicinity of the place of decomposition becomes saturated with carbon dioxide.

In the apparatus of Hüfner,[1] and that lately devised by Dr. Wm. H. Greene,[2] in which the evolved gases are obliged to pass through a long column of the sodium hyprobromite solution, the conditions exist for the complete absorption of the carbon dioxide with the least possible likelihood of error. But, even in employing these apparatus, the theoretical quantity of nitrogen (372 cc. from 1.0 gram of urea) is not obtained, but according to Hüfner only 354.33 cc. at 0° C. and 760 mm. pressure.

Chemical Laboratory, Med. Dept. University of Pennsylvania.

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[1] Zeitschr. f. physiol. Chem. **1**, 350.

[2] Comptes Rendus **97**, 1141.

A CONTRIBUTION TO THE KNOWLEDGE OF THE ACTION OF CACODYLIC ACID ON THE ANIMAL ECONOMY.

BY JOHN MARSHALL AND WALTER D. GREEN.

The only arsenic compounds in which the toxic properties of the arsenic is doubtful are the so-called arsenic-methyl bodies or cacodyl compounds. In the literature of the subject much conflicting testimony exists relative to the poisonous properties of these compounds, and especially concerning one of them, cacodylic acid, which has been selected as the subject of investigation in this paper. Cacodylic acid, $(CH_3)_2AsOOH$, contains 54.35 per cent. of metallic arsenic equal to 71.4 per cent. of arsenious oxide.

According to Bunsen,[1] who in 1843 was one of the first to investigate the action of this substance upon the animal economy, it has been taken in large doses, and is not in the slightest degree poisonous. Prof. Kürschner[2] (quoted by Bunsen) in his researches proved the fact without doubt, and Bunsen's earlier observations upon frogs were fully confirmed. Bunsen[3] injected six grains of cacodylic acid, presumably by means of a syringe with a long tube attached, into the stomach of a rabbit without the evidence of even the slightest distress on the part of the animal. Seven grains of the acid were injected into the jugular vein of a rabbit without injurious effect. Four grains of the acid were, in a manner not described, injected into the lungs of a rabbit and no symptoms of poisoning were developed. Bunsen concluded from these results that, on account of the manner of combination of the arsenic in cacodylic acid, it is deprived of its poisonous properties.

Bunsen[4] injected eight grams (evidently should be grains) of the acid dissolved in water into the jugular vein of a rabbit without producing any unfavorable symptoms.

Schmidt and Chomse[5] made three experiments upon animals with *perfectly pure cacodylic acid*, and found it to possess no poisonous properties. Their first experiment was performed upon a young cat which had not been fed for twenty-four hours. One gram of cacodylic acid was administered in bread-pills. In thirty minutes the animal showed signs of distress and began to vomit, in which vomit nearly all the pills given were ejected. Very little of the pills was dissolved, as the outside only was softened. Fifteen minutes afterwards the vomiting again commenced, and occurred three times in the following forty-five minutes. During the whole time the cat seemed to be quite lively, and only towards the last, on account of the oft-repeated vomiting, did she show signs of distress.

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[1] Annalen der Chemie **46**, 10. [2] Pogg. Ann. **42**, 140. [3] *Ibid.*

[4] Annales de Chimie et Phys., 3 Serie, **8**, 358.

[5] Moleschott's Unters. z. Naturlehre **6**, 122; 1860.

2. One gram of cacodylic acid dissolved in water was introduced into the stomach of a young cat which had been well fed for twelve hours previously. One and three-quarter hours afterwards vomiting began, which continued for fifteen minutes. Soon afterward liquid feces were ejected, and occurred again two and a quarter hours later. During the whole period the cat showed no other symptoms of distress. She afterward ate with great relish.

3. A mare of torpid constitution, but otherwise physiologically normal (pulse 36, respiration 9), was treated with one gram of cacodylic acid in solution thrown into the left jugular vein. Soon after the injection there was an increase in the pulse, which in the fourth hour settled down to 32. Five hours after the injection nothing other than the previous normal condition of the animal was observed, save that the pulse was 32. In every case cacodylic acid was found by them, in the feces and urine, by reducing the acid to cacodylic oxide with phosphorous acid. Schmidt and Chomse concluded from the result of these experiments that cacodylic acid possessed no poisonous properties.

Lebahn,[1] however, who performed a series of experiments under the direction of Prof. Schulze, Sr., declares from the results of his experiments that cacodylic acid does possess poisonous properties, and that its toxic symptoms are like those of ordinary arsenical poisoning. He experimented wholly upon rabbits, and found that all those (10) to whom the acid was administered died.

Lebahn's Experiments.

1. After the administration of 0.071 gram of cacodylic acid, in four separate portions, into the jugular vein, also dissolved in milk and injected under the skin, the animal died in sixteen days.

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[1] Ein Beitrag zur Kenntniss der Wirkung der Kakodylsäure. Dissert., Rostock, 1868.

2. 0.022 gram of the acid given in three portions: twice in milk and once injected under the skin. The animal died in eight days.

3. 0.083 gram of the acid injected under the skin at one time. The animal died in twenty days.

4. 0.166 gram injected under the skin. Animal died in twenty-five days.

5. 0.25 gram injected under the skin. The animal died in eighteen days.

6. 0.2 gram of arsenious oxide injected into the mouth by means of a syringe in two separate portions. Animal died in sixty hours.

7. 0.5 gram of cacodylic acid injected into the mouth. Animal died in ninety-four hours.

8. 0.5 gram of the acid injected into the mouth. Animal died in twenty-three hours.

9. 0.75 gram of the acid injected into the mouth. Animal died in twenty-nine hours.

10. 2.3 grams of the acid, in three portions, injected into the mouth. Animal died in eight days.

Lebahn also found cacodylic acid, as described by Schmidt and Chomse, in the urine and feces by reducing to cacodylic oxide with phosphorous acid.

A quantity of crystalline acid was obtained from a Philadelphia manufacturer of fine chemicals, and the following experiments were performed with one cat and three rabbits:

1.—Sept. 24, 1885. To a young male cat of about 1500 grams weight was administered, at 1.08 P. M., 0.5 gram of cacodylic acid dissolved in about 5 cc. of water. The following effects were produced:

1.45 P. M. Violent retching.
2.35 P. M. Cat vomited. Very sick.
2.40 P. M. Vomited a curdy white material.
2.44 P. M. Vomited a curdy white material.
2.48 P. M. Copious soft, greenish defecation.
2.50 P. M. Marked salivation appeared.
2.52 P. M. Vomited.
2.57 P. M. Vomited and refused to drink water.
3.00 P. M. Copious urination occurred. Cat very restless and in pain. Moaning.

3.10 P. M. Vomited frothy white material. The garlic-like odor due to cacodyl compounds was strongly apparent upon the breath.

The following day (Sept. 25) 0.3 gram of cacodylic acid was given hypodermically to the same cat. Very profuse salivation was immediately noticed. Neither cacodylic acid nor arsenic could be detected in the saliva. The garlic-like odor was again noticed upon the breath. At this juncture the cat escaped, but was recovered two days afterwards in good health.

2.—Sept. 24, 1885. A female rabbit. Weight, about 2500 grams. At 1.30 P. M. 0.1 gram of the acid was administered hypodermically. The animal became very restless. On the following day, Sept. 25, a copious urination occurred at 11.25 A. M. The urine contained jelly-like masses, which under the microscope were found to be mucus. The animal ate food with seeming relish.

3.00 P. M. Urine drawn with a catheter. The presence of cacodylic acid was distinctly determined in it.

3.30 P. M. 0.5 gram of the acid was injected hypodermically. Garlic-like odor was noticed upon the breath. The administration of the acid was stopped. There were no ill effects, except a very noticeable restlessness. The animal entirely recovered.

3.—Sept. 28, 1885. Female rabbit. Weight, 1800 grams.

3.30 P. M. 0.5 gram of the acid was given by the mouth.

4.00 P. M. Salivation noticed. The animal became very sick. No more acid was administered, and the animal fully recovered.

4.—Sept. 29, 1885. Male rabbit. Weight, 1630 grams.

1.00 P. M. Was given 0.5 gram of the acid in solution by the mouth.

1.30 P. M. Animal very restless. Shaking head violently from side to side.

Sept. 30, 1885. Animal ate food readily.

11.25 A. M. Copious discharge of urine, containing jelly-like masses, which proved to be mucus.

1.00 P. M. 0.5 gram of the acid in solution was given by the mouth. Garlic-like odor was very strong on the breath. The animal died during the night.

Post-mortem. Oct. 1, ten hours after death. Stomach full of partly digested grass. Bladder half full of urine. Large intestine greatly distended with liquid colored yellow by feces. The whole alimentary tract showed evidences of a severe gastro-enteritis. Cacodylic acid could not be detected in the brain, but was found in the kidneys. Phosphorous acid was employed to detect the presence of the acid.

It was observed at this juncture that the cacodylic acid that was employed was not entirely soluble in water, a slight residue always remaining undissolved. Upon examining this insoluble residue microscopically, it was found to be composed of perfectly formed octahedral crystals, which on further testing proved to be arsenious oxide. The remainder of the acid was treated with alcohol, which dissolved the larger part of it. The undissolved portion consisted of octahedral crystals of arsenious oxide. The alcoholic solution was filtered, and the filtrate allowed to evaporate at a low temperature. The resulting crystals were again treated with alcohol, and an insoluble residue of crystalline arsenious oxide was again observed. This recrystallisation after filtration was repeated several times, and each time an insoluble residue of arsenious oxide remained. The fact of this contamination of the cacodylic acid with arsenious oxide necessarily vitiates the results obtained in the preceding experiments.

As Lebahn,[1] in his paper, does not refer to the purity of the cacodylic acid employed by him, it may be possible that the acid he used was contaminated with arsenious oxide, and that the death of the animals used in his observations was not produced by cacodylic acid, but by arsenious oxide.

A new series of experiments was now begun with cacodylic acid obtained from Kahlbaum, of Berlin. It was first, however, thoroughly examined concerning its purity.

1. The crystals were colorless and odorless. Easily soluble in alcohol.
2. An aqueous solution reddened blue litmus.
3. Hydrogen sulphide produced in a water solution a white milkiness, which did not disappear upon boiling.
4. Warmed with phosphorous acid a strong odor of cacodyl was produced, and at the same time the evolution of thick, white fumes of cacodyl oxide was observed.
5. The acid in water solution with mercuric chloride gave a white crystalline precipitate of needle-like crystals, which on heating to boiling did not disappear.
6. A water solution of the acid boiled with red mercuric oxide

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[1] *Loc. cit.*

caused no change—*i. e.*, no reduction of mercuric oxide. The filtrate upon cooling was clear, and was not tinged by hydrogen sulphide.

7. The solution of the acid with stannous chloride produced a strong, white cloudiness, and upon warming, a very penetrating odor of cacodyl chloride.

8. Silver nitrate added to a water solution of the acid produced a white precipitate, which on heating turned brown. The liquid had no odor. The precipitate increased upon the addition of ammonium hydroxide, but dissolved in excess of the latter reagent with the production of a brown coloration. Upon boiling this ammoniacal solution a silver mirror was formed, and the liquid became clear and colorless.

9. A water solution of the acid, placed with hydrochloric acid and zinc in a gas-evolution apparatus whose exit-tube led into a solution of silver nitrate, produced a brown, flocculent precipitate in the latter solution, and at the same time, heavy, white fumes were produced in the flask.

10. Barium and calcium hydroxides, calcium chloride and plumbic acetate produced no change in a water solution of the acid.

11. Zinc and platinum in galvanic circuit quickly produced the odor of cacodyl in a water solution of the acid.

It may be taken as conclusive, from the reactions above described, and the physical properties of the crystals employed, that the material was perfectly pure cacodylic acid.

Experiments with Kahlbaum's Cacodylic Acid.

1.—October 10, 1885. A female dog. Weight, 12 kilos.

At 10.35 A. M. 0.5 gram of the acid dissolved in 5 cc. of water was given by the mouth.

10.47 A. M. Vomited. Greatly distressed.

11.05 A. M. 0.5 gram dissolved in 5 cc. of water was given by the mouth. Dog very uneasy. Moaned with pain.

11.27 A. M. Defecated with great pain. Large, dark, loose feces.

12.25 A. M. Vomited curdy white material.

1.15 P. M. 0.1 gram of acid dissolved in 5 cc. of water was given by the mouth. The dog escaped at this juncture, but was recovered three days later in a healthy condition.

November 7, 1885. The dog was kept until this time (twenty-eight days), no more cacodylic acid having been administered since the amount of 0.1 gram given October 10. The animal was killed, and an autopsy made, which showed an evident gastro-enteritis, and also congestion of the liver, lungs and peritoneum.

2.—October 15, 1885. Dog. Weight, 18 kilos. Dog had not been fed for thirty-six hours.

At 10.30 A. M. 0.2 gram of the acid dissolved in 5 cc. of water was given by the mouth.

10.35 A. M. Salivation produced.

10.50 A. M. Vomited green, frothy matter. Breath had garlic-like odor of cacodyl. Dog lively.

11.30 A. M. 0.1 gram dissolved in 5 cc. of water given by mouth. Garlic odor on breath. Dog lively.

12.30 P. M. 0.1 gram administered as above.

1.30 P. M. 0.1 gram administered as above.

2.30 P. M. 0.1 gram administered as above.

3.30 P. M. 0.3 gram administered as above.

4.25 P. M. Dog vomited, and at same time defecated. Feces soft and yellowish, with a strong garlic-like odor. Dog very sick.

4.30 P. M. 0.2 gram administered by mouth. Dog sick.

4.35 P. M. Vomited.

5.30 P. M. 0.1 gram given by mouth. Breath still has garlic-like odor. Dog very sick.

October 16, 1885. Same dog. Fed at 8.30 A. M. Dog lively. Breath still has garlic odor.

11.00 A. M. 0.2 gram dissolved in 5 cc. of water given by mouth.

11.45 A. M. Vomited.

2.00 P. M. 0.1 gram administered by mouth. Garlic odor.

3.00 P. M. 0.1 gram administered by mouth. Garlic odor.

4.00 P. M. 0.1 gram administered by mouth. Garlic odor.

5.00 P. M. 0.1 gram administered by mouth. Garlic odor.

6.00 P. M. 0.1 gram administered by mouth. Garlic odor. Dog defecated during the night. Feces were bloody and mucous-like, with garlic-like odor.

October 17, 1885. Same dog. Fed at 8.30 A. M. Lively in spirits.

11.30 A. M. 0.1 gram dissolved in 5 cc. of water given by mouth.

11.50 A. M. Salivation appeared.

12.00 M. Pulse 103; respiration 17. Defecated light yellow mucous-like feces with a strong garlic odor.

12.30 P. M. 0.1 gram was given in a small piece of meat.

1.30 P. M. 0.1 gram was given in a small piece of meat.

2.30 P. M. 0.1 gram was given in a small piece of meat. Ate a large piece of meat. Dog shows no evidence of distress.

3.30 P. M. 0.1 gram was given in a small piece of meat.

4.30 P. M. 0.1 gram was given in a small piece of meat.

5.30 P. M. 0.1 gram was given in a small piece of meat. Defecated three times during the night. The feces were soft, slimy, mucous-like and streaked with blood.

October 18, 1885. Same dog. Dog lively.

11.00 A. M. 0.2 gram administered in a small piece of meat.

11.35 A. M. Vomited.

12.00 M. 0.2 gram administered in small piece of meat.

1.00 P. M. 0.1 gram administered in small piece of meat.

2.00 P. M. 0.1 gram administered in small piece of meat.

October 22, 1885. Same dog. Condition unchanged. At 1.00 P. M. 3.0 grams of the acid dissolved in 10 cc. of water were injected into the jugular vein.

1.10 P. M. Vomited.

1.15 P. M. Vomited green, slimy material, which when tested was found to contain cacodylic acid. There were no solids in the vomit. Dog had two large liquid defecations.

October 23, 1885. Dog lively. Eyes congested. Long strings of mucus depended from eyelids. Conjunctiva greatly inflamed.

October 31, 1885. Same dog. Condition good. At 1.30 P. M. 2.0 grams of the acid dissolved in 10 cc. of water were injected into the jugular vein.

1.35 P. M. Animal distressed.

1.42 P. M. Vomited slimy, greenish matter, which did not contain cacodylic acid.

1.55 P. M. Vomited slightly. Same material as before. Cacodylic acid was found in this vomit.

2.00 P. M. Animal greatly distressed.

3.00 P. M. 7.0 grams dissolved in 30 cc. of water injected in the jugular vein. No untoward effects were noticed, and fifteen minutes later the dog was killed by severing the spinal cord. Throughout the whole experiment (seven days) the dog's urine was examined for cacodylic acid, which was found in every case. The feces of October 16, 17 and 18, treated separately with distilled water, warmed, filtered, and the filtrate evaporated to dryness at a low temperature, showed the presence of cacodylic acid by giving off a strong cacodylic odor when warmed with phosphorous acid.

Results of Autopsy.—Intense inflammation of the stomach, intestines and lungs. Peritoneum injected. The mucous membranes covered with a thick pus. Intensely congested. Spleen enlarged. Kidneys congested.

Microscopic Examination of the Organs.

Lungs.—The blood-vessel walls were thickened, and their lumen everywhere filled with blood. The small capillaries and veins everywhere congested. Lung tissue generally inflamed. The alveolar walls were thickened by cell infiltration, and many of the air vesicles showed distinct catarrhal change, some being filled with epithelial cells, others with a lymphoid exudation, and still others were infarcted with blood. The appearance of the organs generally was that caused by an acute catarrhal pneumonia. In some of the more intensely inflamed portions there was observed numerous yellow, needle-like and cone-shaped crystals resembling hippuric acid. *Spleen.*—Appeared pigmented, which was probably due to the coloring matter of the blood, either in the shape of hæmin crystals or of an amorphous precipitate. The blood-vessels were all intensely congested, and the trabeculæ of the smooth, muscular tissue appeared unusually thick; otherwise nothing abnormal was observed. *Liver and Stomach.*—Showed cloudy swelling of the cells, due to inflammation. *Kidneys.*—Showed same cloudy swelling and a slight degeneration of the epithelium. Heart muscle did not show any morphological changes, and the blood generally was unaltered.

3.—November 3, 1885. Dog of about 15 kilos. weight.

1.50 P. M. 2.0 grams of the acid dissolved in 15 cc. of water were injected into the jugular vein.

1.55 P. M. Dog distressed.

1.56 P. M. Vomited green, slimy material.

1.58 P. M. Vomited same matter again.

2.00 P. M. Defecated. Feces loose and yellowish.

2.02 P. M. Vomited green, slimy material. A very small amount of cacodylic acid was found in this vomit.

2.10 P. M. Distress disappearing. Dog did not die. He was kept in view for several weeks afterward.

4.—November 14, 1885. Dog of 10 kilos. weight.

12.00 M. 3.0 grams of acid dissolved in 20 cc. of water were injected into the jugular vein.

12.10 P. M. Profuse salivation. Respirations, 180 per minute. Dog very sick. Lies down and is unable to get up.

12.35 P. M. Respirations much slower. Dog very uneasy.

12.38 P. M. Attempts to stand, but falls.

12.40 P. M. Gets up and drinks. Staggering gait. Weakness of whole right side manifest.

November 15, 1885. 10.00 A. M. Dog vomited twice during the night. Both ejections contained cacodylic acid. Dog lively and ate with evident relish. This dog lived several weeks, and was subsequently used for other purposes.

5.—November 7, 1885. Small dog weighing about 5 kilos.

2.00 P. M. 3.0 grams of the acid dissolved in 20 cc. of water were injected into the jugular veins.

2.04 P. M. Vomited a small quantity of slimy, greenish matter. No cacodylic acid was found in this vomit.

2.10 P. M. Extreme salivation. Great pain.

3.10 P. M. Staggering gait. Dog leans to the right side. Tactile sensibility lost. Pupils dilated evenly. Respirations slow and labored. Dog moans as if in pain.

3.40 P. M. Dog rises with much difficulty and immediately falls.

4.45 P. M. Dog died.

The evident cause of death in this experiment was the enormous amount of the acid in proportion to the weight of the dog, which was introduced directly into the circulation. Immediately after injecting the acid the blood-pressure tracings were taken with the kymographion, showing slowing of pulse and decrease in arterial pressure.

Autopsy.—Peritoneum greatly injected. Intestines congested and mucous membrane covered with pus. Lungs congested. Left auricle full of dark, unclotted blood. Urine evaporated to dryness and tested showed presence of cacodylic acid strongly.

According to Schmidt and Stürzwag,[1] upon the administration of arsenious oxide nervous symptoms occur, due to spinal irritation and paralysis. To the spinal irritation may be ascribed the vomiting and slowing of respiration, and also the partial paralysis or convulsive movements. These same symptoms occurred in the foregoing experiments with cacodylic acid, except the paralysis and convulsive movements, which only existed in a slight degree. Schmidt and Stürzwag observed a decided weakness in the hind extremities, so that the animal was unable to stand. The same was observed in the preceding experiments with the acid. Schmidt and Stürzwag also noticed that a peculiar condition of somnolence occurred, in which movements were uncertain. This was also noticed in these experiments with cacodylic acid. The weakness, however, in all cases experimented upon with the acid was unilateral, resembling hemiplegia. In Schmidt and Stürzwag's cases diarrhœa was observed in nearly all the animals. This was noticed in all the experiments in the present investigation.

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[1] Moleschott's Unters. z. Naturlehr. **6**, 296.

Lebahn observed that the action of cacodylic acid and arsenious oxide produce nearly analogous symptoms, and that the pathological changes were the same. The foregoing experiments confirm Lebahn's observations as far as the symptoms are concerned (*i. e.*, the analogous symptoms produced by cacodylic acid and arsenious oxide); but, as has been shown by the experiments described in this paper, cacodylic acid is not fatal in its effects. The fatal terminations in Lebahn's cases were probably due to an impure acid which he may have employed, which, as has been shown in the first part of this paper, may very readily happen. Lebahn concluded from his results that a part of the cacodylic acid was, by the action of the blood, decomposed, and that the arsenic set free entered into combination in its inorganic form with an alkali, and in this manner acted upon the organism. A part of the cacodylic acid may be given off by the lungs as paracacodylic oxide (*vide* the garlic-like odor on breaths), and the rest of it is excreted by means of the urine and feces as cacodylic acid. The formation of paracacodylic oxide may be the cause of the vomiting. Schmidt and Chomse[1] found that by the injection of the acid into the blood no perceptible action was produced. In the experiments described in this paper it may be observed that the action of the acid (causing vomiting, purging, etc.) was the same, whether given by the mouth or injected directly into the circulation. Finally, then, judging from the results of the experiments herein described, it may be concluded that cacodylic acid is not a poisonous substance in the general acceptation of the word poison.

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[1] *Loc. cit.*

ON THE VALUE OF BRÜCKE'S METHOD FOR THE REMOVAL OF INTERFERING SUBSTANCES FROM URINE IN TESTING FOR GLUCOSE.

By Edgar Moore Green.

In determining the presence of glucose in diabetic urine by any of the copper tests it is found that, under certain circumstances, some of the normal constituents of urine, such as creatinine and uric acid, interfere with the reaction of these tests. In the ordinary course of a case of diabetes, when the urine contains an abundance of glucose, usually no difficulty is experienced in obtaining the reactions; but after the patient has been restricted to a diet of nitrogenous food alone, great difficulty is often found in making the tests, because of a diminution in the amount of glucose and an increase in the amount of the interfering substances, creatinine, uric acid, etc. It may therefore be necessary to remove these substances before testing for the glucose. The method for their removal suggested by Brücke, and in use many years, consisted in adding neutral plumbic acetate, $Pb(C_2H_3O_2)_2$, to the urine, and immediately afterward adding plumbic tribasic acetate, $Pb_3O_2(C_2H_3O_2)_2$. The precipitate was then separated by filtration and washed with distilled water. The filtrate and washings having been collected in one vessel, ammonium hydroxide was added, which threw down the glucose in combination with the lead in the form of lead saccharate, $(PbO)_3(C_6H_{12}O_6)_2$. This white precipitate was collected on a filter-paper, washed, and then suspended in distilled water, and hydrogen sulphide, which decomposed the compound, passed through it. The filtered solution contained the glucose;[1] and it was used for the tests, after the hydrogen sulphide had been driven off by evaporation.[2] The original paper by Brücke could not be obtained, as it was not to be found in the journal referred to by Neubauer and Vogel. However, Beale gives the same method as the preceding. According to Bence Jones, "the seventh of a grain of glucose may be detected, when diluted with upwards of six ounces of water, and two-thirds of the total quantity of glucose present in a solution can be separated by this process."[1]

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[1] The neutral plumbic acetate removes the sulphates, phosphates, and carbonates. The plumbic tribasic acetate precipitates the coloring matter, and at least a portion of the uric acid and creatinine. Probably a small amount of uric acid is contained in the precipitate of lead saccharate, and the remainder of the uric acid and creatinine, together with the urea, are contained in the filtrate after removal of the lead saccharate.

[2] Neubauer and Vogel. 8th Ed., 1881, 165.

The method of Brücke, as given by Salkowski and Leube,[2] is as follows: Neutral plumbic acetate is first added to the urine, which is then filtered. Plumbic tribasic acetate and, afterward, ammonium hydroxide are added to the filtrate. After collecting the precipitate on a filter it is washed and suspended in water, hydrogen sulphide passed through it, and the evaporated solution employed for making the tests for glucose.

Although certain statements have been made by different writers as to the amount of glucose recovered after the use of this process, yet, so far as could be learned, no accurate experiments had been made to verify these statements. For this reason the experiments here described were undertaken for the estimation of this amount, and the determination thereby, if possible, of the practical value of the process. For it is readily seen that if a large percentage of the glucose is lost in the procedure, when but a relatively small amount had been present, that which remains may not be sufficient to give the proper reactions. Hence it might be thought that no glucose is present, when it has really been present in the original urine. In making the experiments, fresh normal urine, free from glucose, was used, and to certain quantities of this were added definite amounts of pure crystallised glucose. The first method attempted was the following: Three portions of urine containing definite amounts of glucose were employed: 100 cc. of urine containing 1.0 gram of glucose; 100 cc. of urine containing 0.5 gram of glucose; 100 cc. of urine containing 0.1 gram of glucose. Each of these quantities of urine, after the glucose had been thoroughly dissolved, was then divided into two parts of 50 cc. each, and the two samples worked at the same time. To each of these portions of urine were added 35 cc. of a 10 per cent. solution of neutral plumbic acetate. It was then stirred and filtered, and the precipitate washed with water in six portions of 5 cc. each. The filtrate and wash-water were collected together and stood aside. (For convenience this will be designated filtrate *A*.) The precipitate was suspended in about 50 cc. of water, warmed, and hydrogen sulphide passed through it until all the lead was precipitated, and then filtered. The precipitate was then washed with water in five portions of 5 cc. each, and the filtrate and wash-water evaporated to dryness on a water-bath. The dry residue was extracted with three or more portions of 5 or 8 cc. each of alcohol (to get rid of uric acid). The solution was filtered through a small filter, and the residue washed with about 15 cc. of alcohol. The alcoholic extract with the washings was evaporated to dryness on a water-bath.[1] The dry residue was dissolved in water, the volume of the solution carefully ascertained, and the amount of glucose present determined by means of Fehling's solution or the saccharimeter.

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[1] Beale, "Kidney Diseases, Urinary Deposits and Calculous Disorders." 3d Ed., 249.

[2] "Die Lehre vom Harn." 1882, 224.

To filtrate *A*, obtained after the addition of neutral plumbic acetate to the urine, were added 15 cc. of plumbic tribasic acetate.[2] After being stirred and filtered, the precipitate was washed with water in six portions of 5 cc. each. (The filtrate and wash-water will be designated *B*.) The precipitate was suspended in about 50 cc. of water, warmed, and hydrogen sulphide passed through it until all the lead was precipitated. It was then filtered, and the precipitate washed with water in five portions of 5 cc. each. The filtrate and wash-water, collected together, were evaporated to dryness on a water-bath, the residue extracted with methyl alcohol, filtered, washed with more alcohol, and evaporated to dryness on a water-bath. The dry residue remaining was extracted with water, the volume of the solution ascertained, and the amount of glucose present determined as in the previous instance.

To filtrate *B* with wash-water, obtained after the precipitation by plumbic tribasic acetate, was added ammonium hydroxide until the solution had a slight odor of ammonia. The precipitate thus formed was collected on a filter-paper, washed with water in five portions of 5 cc. each, and the filtrate with the wash-water preserved. (It will be designated filtrate *C*.) The filter-paper was pierced, and the precipitate washed into a beaker and diluted with water to a volume of about 100 cc., the mixture warmed, and hydrogen sulphide passed through until all the lead was thrown down. The precipitate was collected on a filter and washed with five portions of water of 5 cc. each; the filtrate and wash-water collected together, evaporated to dryness, extracted with methyl alcohol, filtered and washed, evaporated to dryness, extracted with water, and the amount of glucose determined as before. (The amount of glucose found in this instance should be the amount present at the end of the process, while amounts found in each of the other instances would be the losses occasioned by the process.) Filtrate *C*, with the wash-water obtained after the addition of ammonium hydroxide, was evaporated to dryness, and after being treated as in the other instances, the glucose present was estimated by Fehling's solution or by the saccharimeter.

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[1] Methyl alcohol was here used, glucose being more soluble in it than in the ordinary ethyl alcohol. All the alcohol used was first tested carefully to be sure that it contained no reducing substance, by evaporating a portion to dryness on a water-bath, dissolving the residue in water, and testing it by means of Fehling's solution.

[2] Prepared as follows: 192 grams of acetate of lead were dissolved in 640 cc. of distilled water, and 64 grams of yellow oxide of lead added. This was allowed to stand (with frequent shaking), until only a small white precipitate remained. The precipitate was then removed by filtration, and the solution was ready for use, its specific gravity being between 1.23 and 1.24.

Certain difficulties, however, were found in this process which rendered it impracticable. It was found, after evaporating the various solutions to dryness, even though done on a water-bath and with greatest care at a low temperature, that a dark brown, or at times almost black, residue was obtained; which partly dissolved in the alcohol, and rendered the final water solution so dark that it could not be used in the saccharimeter, even in some instances preventing the passage of any light at all through the observation tube. The color of the solution also prevented the use of Fehling's solution, for when it was added to the latter reagent a green solution was obtained, and the exact point of the completion of the reaction could not be determined. On account of the very dark color of the solution it was not possible to dissipate the color sufficiently by dilution without carrying it to such a degree that the small amount of glucose present could not be detected. It was thought that the dark color was probably produced by concentration (during evaporation) of the coloring matters of the urine. It was also thought that the acid found to be present in the solution might produce some reaction on certain of the urinary constituents present and thus cause a dark coloration. Therefore, after the excess of hydrogen sulphide had been driven off by evaporation on a water-bath, a saturated solution of sodium bicarbonate was added, until the solution was rendered neutral, and the evaporation then continued to dryness. It was found, however, that this neutralisation of the acid did not prevent the formation of the dark residue, and hence this method was abandoned.

The method next adopted was to make a number of solutions by dissolving a definite quantity of glucose in a small amount of urine, and then adding more urine until a volume of 100 cc. was obtained. A number of such solutions were made of different strengths, so that 100 cc. would contain 0.05 gram, 0.1 gram, 0.5 gram, 1.0 gram, or 2.0 grams of glucose. Then the strength of each solution was 0.05 per cent., 0.1 per cent., 0.5 per cent., 1.0 per cent., or 2.0 per cent. Each solution was then carefully divided into two parts of 50 cc. each by means of an accurate pipette. In this way two solutions of exactly equal strength were obtained, which could be readily carried through the process at the same time. (In the following description each solution mentioned is to be understood as having had a volume of 50 cc.) To each portion of urine were added 20 cc. of a 10 per cent. solution of neutral plumbic acetate. The mixture was thoroughly stirred and afterwards filtered, and the precipitate washed with 25 cc. of distilled water in portions of 5 cc. each. The filtrate and washings having been collected together, were poured into a graduated cylinder, the volume of the whole ascertained, and the amount of glucose present determined by taking the average of at least ten observations with the saccharimeter. The saccharimeter tube was carefully washed out, the washings saved and placed with the remainder of the solution, to which were then added 15 cc. of plumbic tribasic acetate, the mixture carefully stirred and filtered, and the precipitate washed with 25 cc. of distilled water in portions of 5 cc. each. The filtrate and washings having been collected together, the volume of the whole solution was ascertained, and the amount of glucose present estimated by the saccharimeter as before. To the whole of this solution, which was carefully saved after the estimation, were added 20 cc. of ammonium hydroxide,[1] and the mixture carefully stirred and filtered. The precipitate was washed with 25 cc. of distilled water in portions of 5 cc. each, and the filtrate and wash-water collected, the volume of the whole ascertained, and the amount of glucose present determined by the saccharimeter.

The precipitate caused by the addition of ammonium hydroxide was suspended in distilled water, and hydrogen sulphide passed through it until all the lead was precipitated, then filtered, and the precipitate washed with 25 cc. of distilled water in portions of 5 cc. each. The filtrate and wash-water were collected together, the volume of the whole solution ascertained, and by the saccharimeter the amount of glucose present was determined.

In three cases a saturated solution of potassium carbonate instead of hydrogen sulphide was used to decompose the lead saccharate.

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[1] The solution of ammonium hydroxide employed contained 10 per cent. of NH_3.

In several cases, both neutral plumbic acetate and plumbic tribasic acetate were added before filtration, and the proportion of glucose present then determined, after which the process was carried on as before described.

In a few instances one or more of the determinations were made by Fehling's solution instead of by the saccharimeter.

In some of the solutions the quantity of glucose was not estimated until after the completion of the whole process. Frequently, however, an estimation was also made of the glucose lost in the filtrate after precipitation by ammonium hydroxide.

By these different methods almost all possible conditions of working the original process were obtained, and it was possible to ascertain not only the whole amount of loss caused by the process, but also the steps which involved a loss, and the amount of each.

The saccharimeter used in these experiments was one of the latest Laurent shadow instruments of the largest size.

The 200 mm. tube was frequently used, but when testing a weak solution the 400 mm. tube was used. In every case at least ten observations were made, and the average of these was adopted as showing the amount of glucose present. The glucose was perfectly pure, crystallised and anhydrous, polarising 99.85° to the right as shown by previous experiment.

In two solutions containing 0.05 per cent. of glucose, the average loss caused by the process was found to be 41.00 per cent., the tests being made by Fehling's solution.[1]

A solution containing 0.1 per cent. of glucose showed a loss of 52.60 per cent. by the neutral plumbic acetate and plumbic tribasic acetate, when both were added before the first filtration, and a loss of 66.80 per cent. by the whole process, leaving 14.20 per cent. as the loss caused by the precipitations by ammonium hydroxide and by hydrogen sulphide. However, as only a trace of glucose was found in the filtrate and washings obtained after the precipitation by ammonium hydroxide, this loss must have been caused almost entirely by the precipitation by hydrogen sulphide. In one solution containing the same amount of glucose, only 2.60 per cent. was lost as determined by Fehling's solution in employing the method, and only a trace of glucose was found in the filtrate and washings obtained after precipitation by ammonium hydroxide. In four solutions of the above strength, no glucose was found in the filtrate and washings obtained after precipitation by ammonium hydroxide. The average loss in the six solutions employed, containing this amount (0.1 per cent.) of glucose, was 59.16 per cent.

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[1] In the estimations following, the saccharimeter was invariably used, unless Fehling's solution is specially mentioned as having been employed.

In two solutions, containing 0.5 per cent. glucose, it was found that the average loss in the precipitation by neutral plumbic acetate was 28.22 per cent., while in the precipitation by plumbic tribasic acetate it was 2.76 per cent., making the loss in the two precipitates 30.98 per cent. In the same solutions the average loss by the whole process, as determined by Fehling's solution, was 50.26 per cent., leaving a loss of 19.28 per cent. to be accounted for by the precipitation by ammonium hydroxide and by hydrogen sulphide. But the average loss found in the filtrates obtained after precipitation by ammonium hydroxide was 6.85 per cent., so that the loss caused in the precipitation by hydrogen sulphide was 12.70 per cent. In two solutions, containing the same amount of glucose, both neutral plumbic acetate and plumbic tribasic acetate were added before the first filtration, and the average loss was then found to be 37.82 per cent., and the loss by the whole process was 54.46 per cent., leaving 16.64 per cent. as the loss occasioned by ammonium hydroxide and hydrogen sulphide; but no glucose was found in the filtrates obtained after precipitation by ammonium hydroxide, so that this percentage must represent the loss in the precipitation by hydrogen sulphide. In two solutions, also of this strength, the total loss was found to be 40.20 per cent., both neutral plumbic acetate and plumbic tribasic acetate having been added before filtration. From the six solutions of this strength (0.5 per cent.), the average loss occasioned by the process was 47.33 per cent., while in four of them the loss caused by neutral plumbic acetate and by plumbic tribasic acetate was 34.40 per cent., and the loss to be accounted for by the precipitation by ammonium hydroxide and hydrogen sulphide was 17.96 per cent. But the average loss caused by ammonium hydroxide was 3.29 per cent., leaving 14.67 per cent. as the average loss occasioned by hydrogen sulphide.

In two solutions, containing 1.0 per cent. of glucose, the loss occasioned by neutral plumbic acetate was 8.09 per cent., and that occasioned by plumbic tribasic acetate was 6.85 per cent., making the total loss up to this part of the process 14.94 per cent. After the addition of ammonium hydroxide to these solutions the lead was removed from one of them by a saturated solution of potassium carbonate, and the total loss of glucose was found to be 76.10 per cent., a loss of 62.90 per cent. having been caused by ammonium hydroxide and by the solution of potassium carbonate. No glucose being found in the filtrate from the precipitation by ammonium hydroxide, this average must represent the loss taking place in the precipitation of the lead by potassium carbonate. From the other solution the lead was removed by hydrogen sulphide, and the total loss of glucose was 49.98 per cent., the loss caused by the precipitation by ammonium hydroxide and hydrogen sulphide being 33.30 per cent. But as 8.34 per cent. was found in the filtrate after precipitation by ammonium hydroxide, the remainder (24.98 per cent.) must have been caused by hydrogen sulphide. In a third solution a loss of 30.02 per cent. was caused by the precipitations by ammonium hydroxide and by hydrogen sulphide, and a loss of 40.34 per cent. by the whole process, a loss of 2.02 per cent. by the precipitation by ammonium hydroxide, and this taken from 10.32 per cent., which was the loss occasioned by both ammonium hydroxide and hydrogen sulphide, leaves 8.30 per cent. as the loss caused by the latter. In two solutions, also containing 1.0 per cent. of glucose, the average loss occasioned by the whole process was 64.33 per cent., and the average loss in the five solutions, from which the lead was removed by hydrogen sulphide, was 50.87 per cent.

The loss caused by neutral plumbic acetate in two solutions, containing 2.0 per cent. of glucose, was 8.30 per cent., and that caused by plumbic tribasic acetate was 8.28 per cent., the sum of these losses being 16.58 per cent., while the whole loss was 75.60 per cent., the lead having been precipitated by a saturated solution of potassium carbonate, leaving a loss of 59.02 per cent., which was caused by ammonium hydroxide and by potassium carbonate. By testing the filtrate obtained after precipitation by ammonium hydroxide, a loss was found in one case of 57.82 per cent., and in the other of 20.89 per cent., making an average for the two of 39.35 per cent., which would leave a loss of 19.67 per cent., which must have taken place in the precipitation by potassium carbonate. In two solutions, also containing 2.0 per cent. of glucose, the average total loss was 52.30 per cent., the lead having been precipitated by hydrogen sulphide.

By referring to Table I, it is seen that in one of these solutions (*V*) hardly any loss took place at this part of the process that was not accounted for. If the loss caused by both neutral plumbic acetate and by plumbic tribasic acetate (17.44 per cent.) be subtracted from the total (75.60 per cent.) loss, 58.16 per cent. is left to be accounted for by ammonium hydroxide and by potassium carbonate. But in the filtrate obtained after precipitation by ammonium hydroxide, 57.82 per cent. of the total amount of glucose was found, leaving only 0.34 per cent. which has not been accounted for. In another solution (*W*) it is observed that although a loss of 59.89 per cent. must have been caused by ammonium hydroxide and by potassium carbonate, yet only 20.89 per cent. was found in the filtrate after precipitation by ammonium hydroxide, and hence there still remains to be accounted for 39.00 per cent. It was thought that some glucose might have been lost in the precipitate caused by the addition of a solution of potassium carbonate, and hence in each case this precipitate was diffused in water, and hydrogen sulphide passed through it until all the lead was precipitated. The precipitate of lead sulphide was collected by filtration, and washed with 25 cc. of water in five portions of 5 cc. each. The filtrate and washings were tested, but no glucose was found. However, before passing hydrogen sulphide through the precipitate of lead carbonate diffused in water, the mixture was warmed on a water-bath, and it was then noticed that a dark coloration appeared. No doubt this was caused by the action of an excess of alkali on the glucose present, causing the formation of melassic acid, etc.

By examination of the tables it will be seen that the process does not give satisfactory results if the lead is precipitated by a saturated solution of potassium carbonate, for in the three solutions in which it was tried the average loss was 75.77 per cent. The average loss discovered in the filtrates obtained after precipitation by ammonium hydroxide was 26.23 per cent., leaving 49.54 per cent. as the percentage probably lost in the precipitation caused by the solution of potassium carbonate.

It is evident, then, that less than 25.00 per cent. of the glucose, originally present in the urine, can be expected to be found after employing the process in this way.

It is also evident that in all of the processes employed there is a steady loss taking place throughout. By referring to Table III it is observed that after precipitation by neutral plumbic acetate, in two solutions, containing each 0.25 gram of glucose, only 71.78 per cent. was recovered; and in two solutions containing 0.5 gram of glucose only 91.91 per cent., and in two solutions containing 1.0 gram of glucose, 91.70 per cent. was recovered, giving an average of 85.13 per cent. recovered in the six solutions tested.

After precipitation by plumbic tribasic acetate in one solution, containing 0.05 gram of glucose, 47.40 per cent. was recovered. In four solutions, each containing 0.25 gram, 65.60 per cent. was recovered. In three solutions, each containing 0.5 gram, 80.04 per cent. was recovered, and in two solutions, each containing 1.0 gram, 83.42 per cent. was recovered. In these ten solutions, then, the average amount recovered was 71.67 per cent.

At the end of the process in two solutions, each containing 0.025 gram of glucose, 59.00 per cent. was recovered. In six solutions, each of which contained 0.05 gram of glucose, 40.84 per cent. was recovered. In six solutions, each of which contained 0.25 gram, 51.69 per cent. was recovered. In five solutions, each of which contained 0.5 gram of glucose, 49.13 per cent., and in two solutions, each containing 1.0 gram of glucose, 47.70 per cent. was recovered.

When hydrogen sulphide is used to precipitate the lead, it is certain that no one step in the process can be said to be specially faulty. The loss occasioned by the precipitation by neutral plumbic acetate (as seen by Table V) is greater than that caused by plumbic tribasic acetate, but neither of these losses is equal to that which takes place at later steps in the process.

Moreover, the losses are not uniform, but very variable in different solutions. And in the experiments this variation was found to exist, even though the solutions were subjected to exactly the same conditions, and even when the corresponding precipitates, in each case, were washed the same number of times and with equal volumes of water. Hence, from any amount of glucose found after employing the process, it could not be determined how much had originally been present in the urine.

The process certainly removes the interfering substances from the urine; but even for qualitative work, if no reaction for glucose could be obtained after making use of the process, it would be by no means certain that no glucose had been originally present in the urine.

In completing this paper the writer desires to express his great indebtedness to Dr. John Marshall, Demonstrator of Chemistry in the Medical Department of the University of Pennsylvania, for his valuable suggestions in carrying on the work, and to whom any success attained in the experiments is largely due.

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TABLE I.—*Showing Loss after Each Step of the Process and Per Cent. of that Loss.*

	Cc. of Solution Employed.	Amount of Glucose Present.	Loss after Plumbic Acetate.	Per Cent. of Previous Loss.	Loss Caused by Tribasic Acetate.	Per Cent. of Loss.	Sum of Previous Losses.	Per Cent. of Losses.	Total Loss.	Per Cent. of Total Loss.	Amount Finally Present.	Amount Finally Present when K_2CO_3 was used.	Loss in NH_4OH Filtrate.	Per Cent. of Loss.	Loss caused by NH_4HO, H_2S or K_2CO_3 (Estimated).	Per Cent. of Loss.
A	50	0.025	......	......	......	......	......	......	0.0097	38.80	0.0153[1]	......	......	......	......	......
B	50	0.025	......	......	......	......	......	......	0.0108	43.20	0.0142[1]	......	......	......	......	......
C	50	0.05	......	......	......	......	......	......	0.0305	61.00	0.0195	......	0	......	......	......
D	50	0.05	......	......	......	......	......	......	0.0419	83.80	0.0081	......	0	......	......	......
E	50	0.05	......	......	......	......	......	......	0.0013	2.60	0.0487[1]	......	Trace.	......	......	......
F	50	0.05	......	......	......	......	0.0263	52.60	0.0334	66.80	0.0166	......	Trace.	......	0.0071	14.20
G	50	0.05	......	......	......	......	......	......	0.0354	70.80	0.0146	......	0	......	......	......
H	50	0.05	......	......	......	......	......	......	0.0350	70.00	0.0150	......	0	......	......	......
I	50	0.25	0.0808	32.32	0.0039	1.56	0.0847	33.88	0.1263	50.52	0.1237[1]	......	0.0141	5.64	0.0416	16.64
J	50	0.25	0.0603	24.12	0.0099	3.96	0.0702	28.08	0.1250	50.00	0.1250[1]	......	0.0188	7.52	0.0548	21.92
K	50	0.25	......	......	......	......	0.0944	37.76	0.1110	44.40	0.1390	......	0	......	0.0160	6.64
L	50	0.25	......	......	......	......	0.0947	37.88	0.1613	64.52	0.0887	......	0	......	0.0666	26.64
M	50	0.25	......	......	......	......	......	......	0.1126	45.04	0.1374	......	......	......	......	......
N	50	0.25	......	......	......	......	......	......	0.0884	35.36	0.1616	......	......	......	......	......
O	50	0.5	0.0351	7.02	0.0309	6.18	0.0660	13.20	0.3805	76.10	......	0.1195	0	......	0.3145	62.90
P	50	0.5	0.0458	9.16	0.0376	7.52	0.0834	16.68	0.2499	49.98	0.2501	......	0.0417	8.34	0.1665	33.32
R	50	0.5	......	......	......	......	0.1501	30.02	0.2017	40.34	0.2983	......	0.0101	2.02	0.0516	10.32
S	50	0.5	......	......	......	......	......	......	0.1718	34.36	0.3282	......	......	......	......	......
T	50	0.5	......	......	......	......	......	......	0.2856	57.12	0.2144	......	......	......	......	......
U	50	0.5	......	......	......	......	......	......	0.3627	72.54	0.1373	......	......	......	......	......
V	50	1.0	0.1157	11.57	0.0587	5.87	0.1744	17.44	0.7560	75.60	......	0.2440	0.5782	57.82	0.5816	58.16
W	50	1.0	0.0504	5.04	0.1068	10.68	0.1572	15.72	0.7561	75.61	......	0.2439	0.2089	20.89	0.5989	59.89
X	50	1.0	......	......	......	......	......	......	0.4919	49.19	0.5081	......	......	......	......	......
Y	50	1.0	......	......	......	......	......	......	0.5560	55.60	0.4440	......	......	......	......	......

[1] These estimations were made by means of Fehling's solution.

Number of Solutions represented in Averages.	Corresponding Solutions in Table I.	Amount of Glucose in each Solution.	Amount Present after use of Lead Acetate.	Loss.	Amount Present after use of Tribasic Acetate.	Averages of Amounts Present.	Loss.	Averages of Loss.	Amount Finally Present.	Averages of Amounts Finally Present.	Final Losses.	Averages of Final Losses.	Number of Solutions represented in Previous Averages.
2	A, B	0.025	......	......	......	......	......	......	0.0147	0.0147	0.0103	0.0103	2
1	F	0.05	......	......	0.0237	0.0237	0.0263	0.0263	0.0166	0.0204	0.0334	0.0296	6
5	C, D, E, G, H	0.05	......	......	......	......	......	......	0.0212		0.0288		
2	I, J	0.25	0.1794	0.0706	0.1725	0.1639	0.0775	0.0861	0.1243	0.1292	0.1257	0.1208	6
2	K, L	0.25	......	......	0.1554		0.0946		0.1138		0.1362		
2	M, N	0.25	......	......	......	......	......	......	0.1495		0.1005		
2	O, P	0.5	0.4595	0.0405	0.4253	0.4001	0.0747	0.0999	[1]0.2501	0.2456	0.2499	0.2544	5
1	R	0.5	.....	......	0.3499		0.1501		0.2983		0.2017		
3	S, T, U	0.5	......	......	......	......	......	......	0.2266		0.2734		
2	V, W	1.0	0.9170	0.0830	0.8342	0.8342	0.1658	0.1658	[2]0.2440	......	0.7560		
2	X, Y	1.0	......	......	......	......	......	......	0.4760	0.4760	0.5240	0.5240	2

[1] 0.2501 is the amount recovered in *one* of the solutions. The other solution was not considered, as in it the lead was precipitated by K_2CO_3 instead of by H_2S.

[2] 0.2440 was not used in making up the average, as in these solutions the lead was precipitated by K_2CO_3.

TABLE III.—*Averages of the Percentages Recovered and Lost at Different Stages of the Process.*

Number of Solutions represented in the Averages.	Corresponding Solutions in Table I.	Amount of Glucose in each Solution.	Per Cent. Present after use of Lead Acetate.	Per Cent. of Loss.	Per Cent. Present after use of Tribasic Acetate.	Averages of percentages Present.	Per cent. of Losses.	Average of per-cent'gcs Lost.	Percentage Finally Present.	Average percentage Finally Present.	Per Cent. of Total Losses.	Average Per Cent. of Total Losses.	Number of Solutions represented in Previous Averages.
2	A, B	0.025	......	......	......	......	......	......	59.00	59.00	41.00	41.00	2
1	F	0.05	......	.....	47.40	47.40	52.60	52.60	33.20	40.84	66.80	59.16	6
5	C, D, E, G, H	0.05	......	......	......	......	.....	......	42.36		57.64		
2	I, J	0.25	71.78	28.22	69.02	65.60	30.98	34.40	49.74	51.69	50.26	48.31	6
2	K, L	0.25	......	......	62.18		37.82		45.54		54.46		
2	M, N	0.25	.. ...	.....	......	......	......	......	59.80		40.20		
2	O, P	0.5	91.91	8.09	85.06	80.04	14.94	19.96	[1]50.02	49.13	[1]49.98	50.87	5
1	R	0.5	......	......	69.98		30.02		59.66		40.34		
3	S, T, U	0.5	......	......	......	......	......	......	45.32		54.67		
2	V, W	1.0	91.70	8.30	83.42	83.42	16.58	16.58	[2]24.40	......	75.60		
2	X, Y	1.0	......	......	......	. ...	......	......	47.60	47.60	52.40	52.40	2

[1] 50.02 is the percentage recovered in one of the solutions. The other solution was not considered, as in it the lead was precipitated by K_2CO_3 instead of by H_2S.

[2] In these solutions the lead was precipitated by K_2CO_3 and 24.40 per cent. was not considered in making up the average.

TABLE IV.—*Amount of Glucose Present in Each Solution after Each Step in the Process.*

	Volume of each Solution.	Amount of Glucose in each.	Amount Present after use of Lead Acetate.	Amount Present after the use of Tribasic Acetate.	Final Amount Present.	Final Amount Present when K_2CO_3 was used.
A	50 cc.	0.025	......	......	0.0153 (F)	......
B	50 cc.	0.025	......	......	0.0142 (F)	......
C	50 cc.	0.05	......	......	0.0195	......
D	50 cc.	0.05	......	......	0.0081	......
E	50 cc.	0.05	......	......	0.0487 (F)	......
F	50 cc.	0.05	......	0.0237	0.0166	......
G	50 cc.	0.05	......	......	0.0146	......
H	50 cc.	0.05	.....	......	0.0150	......
I	50 cc.	0.25	0.1692	0.1653	0.1237 (F)	......
J	50 cc.	0.25	0.1897	0.1798	0.1250 (F)	......
K	50 cc.	0.25	......	0.1556	0.1390	......
L	50 cc.	0.25	......	0.1553	0.0887	......
M	50 cc.	0.25	......	......	0.1374	......
N	50 cc.	0.25	......	......	0.1616	......
O	50 cc.	0.5	0.4649	0.4340	......	0.1195
P	50 cc.	0.5	0.4542	0.4166	0.2501	......
R	50 cc.	0.5	......	0.3499	0.2983	......
S	50 cc.	0.5	......	......	0.3282	......
T	50 cc.	0.5	......	......	0.2144	......
U	50 cc.	0.5	.....	......	0.1373	......
V	50 cc.	1.0	0.8843	0.8256	......	0.2440
W	50 cc.	1.0	0.9496	0.8428	......	0.2439
X	50 cc.	1.0	......	......	0.5081	......
Y	50 cc.	1.0	......	......	0.4440	......

(F) These results were obtained by the use of Fehling's solution.

TABLE V.—*Average Percentages of Losses Caused at Different Stages of the Process.*

No. of Solutions.	Percentage of each.	Amount of Glucose in each.	Average Loss after use of Lead Acetate.	Average Loss caused by use of Tribasic Acetate.	Sum of these Losses.
2	0.5	0.25	28.22	2.76	30.98
2	1.0	0.5	8.09	6.85	14.94
2	2.0	1.0	8.30	8.28	16.58
Average of above losses.........			14.87	5.96	20.83

TABLE VI.—*Average Percentages of Losses at Different Stages of the Process in all of the Solutions.*

No. of Solutions.	Amount of Glucose Present after use of Lead Acetate.	Loss after Lead Acetate.	Per Cent. of Loss by Tribasic Acetate.	Per Cent. of Amount Present after Tribasic Acetate.	Sum of Previous Losses.	Per Cent. of Total Loss.	Per Cent. Finally Present.
6	85.13	14.87	5.96	79.17	20.83	.....	......
4	......	.....	......	60.44	39.56	......	......
	Average of above percentages			71.67	28.33	52.36[1]	47.64
14						50.52	49.48
	Average of above percentages[2]............					51.71	48.29

TABLE VII.—*Average Amounts of Glucose Recovered after the Process, with Percentages.*

No. of Solutions.	Per Cent. of Glucose in each Solution.	Amount of Glucose in Grams in each Solution.	Amount of Glucose Recovered.	Per Cent. of Glucose Recovered.
2	0.05	0.025	0.0147	59.00
6	0.1	0.05	0.0204	40.84
6	0.5	0.25	0.1292	51.69
5	1.0	0.5	0.2456	49.13
2	2.0	1.0	0.4760	47.60

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[1] Only seven of the solutions were considered in making this average, as in the remaining three of the ten solutions the lead was precipitated by K_2CO_3 instead of by H_2S.

[2] Viz.: in all of the twenty-one solutions employed, in which the lead was precipitated by hydrogen sulphide.

Vol. VIII. [June, 1886.] No. 3.

AMERICAN

CHEMICAL JOURNAL.

ON THE CHANGES EFFECTED BY HEAT IN THE CONSTITUTION OF ETHYLENE.[1]

By D. T. Day.

Many of the simpler phenomena of destructive distillation have been observed during the study of such substances as marsh gas and ethylene. The comparatively simple constitution of these compounds has led to the belief that their decomposition by heat would yield well-defined reactions, from which valuable generalisations might be drawn. Definite statements are accordingly made in many text-books concerning the action of heat upon ethylene; but comparison of them shows much that is inconsistent, arising, doubtless, from the fact that this point has entered as a secondary feature in many investigations on other themes, leaving the literature in a somewhat confused state. In attempting to use the effect of heat upon ethylene as the starting-point of another investigation, it became necessary to collect the scattered literature and to supplement it by the following work, in which some new facts have been developed.

When the Dutch chemists Deimann, Van Troostwyk, Lauwerenburg and Bondt[2] first recognised the difference between ethylene and marsh gas, they tried to fix the conditions under which ethylene is formed by heating the vapor of alcohol, and for this purpose examined the action of heat upon ethylene. They stated that, 1. ethylene when heated did not decrease in volume; 2. it lost the property of forming an oily liquid with chlorine; 3. the tube in which it was heated was blackened and covered by drops of empyreumatic oil. At the request of the Philomathean Society of Paris, Fourcroy, Hecht and Vauquelin[1] repeated some of these experiments, and showed that at high temperatures ethylene yields a considerable proportion of hydrogen, carbon is deposited, and no ethylene remains unchanged.

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[1] From the Author's Thesis for the Degree of Doctor of Philosophy in the Johns Hopkins University.

[2] Annales de Chimie et de Physique, 1st series, **21**, 48; Nicholson's Journal **1**, 44; Gilbert's Annalen **2**, 201.

The formation of ethylene during the dry distillation of many organic bodies was noticed by William Henry[2] in 1805, who also noted the fact that ethylene can yield the other common products of dry distillation when further heated. He showed,[3] also, that by passing electric sparks through ethylene for a sufficient time the volume increased, and on exploding the gas with oxygen less carbon dioxide was obtained than before the sparks had been passed. By calculating from the deficit of carbon dioxide the amount of ethylene which had disappeared, it was shown that the increase in volume was equal to twice the volume of ethylene which disappeared. The reaction was not complete, but it showed that all the ethylene which entered into the reaction decomposed smoothly into carbon and hydrogen; thus:

$$C_2H_4 = C_2 + 2H_2.$$

This view was supported by the deposition of carbon in the tube. No secondary products were formed, for if they had been, they would have caused some contraction, and the carbon in them would have appeared as carbon dioxide in the subsequent analysis, so that the expansion would not have been twice the loss in carbon. These experiments were practically duplicated some years afterwards by Quet,[4] who passed sparks from an induction coil through ethylene. Carbon was deposited in the line of the sparks, so that eventually a bridge of carbon was formed between the electrodes.

The most complete investigation of the decomposition of ethylene at the temperature of the electric arc was made by H. Buff and

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[1] Gilbert's Annalen **2**, 210.

[2] Nicholson's Journal **10**, 65.

[3] Philosophical Transactions 1809, 446.

[4] Comptes Rendus de l'Academie des Sciences de Paris **42**, 903.

A. W. Hofmann[1] in 1860. By subjecting ethylene to red heat by means of a platinum wire traversed by a powerful current, they obtained a deposition of carbon, but no increase in volume—*i. e.*, marsh gas was formed according to the following reaction:

$$C_2H_4 = CH_4 + C.$$

The marsh gas thus formed remained unchanged at a red heat, but with the electric arc the decomposition went farther, as indicated by a permanent expansion of the gas. With electric sparks the effect was similar: the volume increased rapidly at first, then slowly. In twenty-five minutes the expansion ceased, after 7 cubic centimetres of dry ethylene had become 12.25 cubic centimetres. A bridge of carbon formed between the poles. The residual gas was hydrogen, which had an unpleasant odor and burned with a slightly luminous flame. They were careful to observe that no marsh gas was formed at this temperature.

The experiments mentioned thus far deal principally with the action of electric sparks upon ethylene. They seem to justify the following general conclusions in regard to the action of heat at the highest temperatures which it is convenient to use. The results of Henry's experiments, and, to some extent, those of the Dutch chemists, are in accordance with the conclusion expressed by Fourcroy, Hecht and Vauquelin, that the higher the temperature the greater the tendency for ethylene to yield carbon and hydrogen. The final result of heating by electric sparks is a separation of the gas into its constituents. The question arises whether this is effected by a simple separation of carbon and hydrogen, or whether the decomposition takes place in different stages, such as the formation of marsh gas and carbon, and by successive decompositions results finally in simple carbon and hydrogen. The experiments of Buff and Hofmann, as far as we can interpret them, seem to justify the conclusion that, at the highest temperatures, there is simple separation of carbon and hydrogen; for, although working with this point in view, they failed to obtain secondary products when the highest temperatures were used. No secondary products have been observed by any one, when passing electric sparks through ethylene, except De Wilde,[2] who found small quantities of acetylene; but Berthelot has obtained traces of acetylene from carbon and hydrogen alone under these conditions. The experiments of Henry support the above conclusion, for although the decomposition was by no means complete, the only products obtained were carbon and hydrogen, together with undecomposed ethylene.

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[1] Liebig's Annalen der Chemie **113**, 129.

[2] Zeitschrift für Chemie, 1866, 735.

At temperatures lower than that of the electric arc the decomposition of ethylene is not so simple. This is indicated by the experiments of the Dutch chemists, of Grove, and of Buff and Hofmann to which reference has been made. The latter chemists obtained marsh gas and carbon by use of a heated platinum wire. The experiments of Grove[1] are not in strict accordance with this, but as the spirals were not necessarily heated to the same temperature, perfect agreement could not be expected. The experiments indicate, however, that the next stage preceding complete separation is a decomposition into marsh gas, without the formation of any more complex products.

Passing to still lower temperatures it is difficult to reconcile the statements of different observers as to the products formed, partly because the temperatures were not carefully observed, and distinctions are only made as to the conduct of ethylene at such temperatures as "red heat" and "white heat," while observations at still lower temperatures are altogether wanting. Usually a glass or porcelain tube is heated at temperatures varying from a "low red heat" to white heat; ethylene is passed through this tube and is examined as it issues from the other end. In this way Marchand, Magnus and Berthelot accumulated data for the principal statements made in modern text-books.

Marchand[2] passed ethylene through glass and earthenware tubes filled with fragments of earthenware heated strongly. He analysed the resulting gas by passing it over heated copper oxide and determining the carbonic acid and water as in an ordinary combustion. He stated that when the tube is heated to redness marsh gas and carbon result; at a white heat only carbon and hydrogen. His data for these conclusions are furnished by the proportion of carbon to hydrogen in gas heated to redness and collected at the other end of the heated tube at intervals of thirty to fifty minutes. At first the proportion of carbon to hydrogen was 100 carbon to 17.236 hydrogen. This represents nearly pure ethylene (100 : 16.67); the last collected corresponds (100 : 27.251) to a mixture of marsh gas and ethylene, or at least to marsh gas and some compound richer in carbon than marsh gas. There is no proof that marsh gas was actually formed, except that on heating higher nearly the proportion of marsh gas was reached—*i. e.*, 100 carbon to 30.771 hydrogen. After heating at a strong white heat the carbon nearly disappeared—that is, for 100 parts carbon 6121.2 parts hydrogen were found. These results were confirmed and extended by Magnus,[1] who, in 1847, carefully investigated these phenomena. His main point was that, besides the gaseous products obtained by previous observers, liquids which he speaks of generically as " tar " are also formed when ethylene is passed through a glass tube heated to redness. Except the meagre statement of the Dutch chemists, this is the first observation of the formation of more complex products from ethylene by heat. Magnus states that ethylene (which he prepared by Mitscherlich's method and purified by passing through sulphuric acid and then through caustic potassa) heated to " incandescence " for some time in a glass tube yields tar, but when the upper part of a bent glass tube or bell jar was filled with pure ethylene and heated in a bath of easily fusible metal, " the temperature was little higher than that of boiling mercury," the gas did not have the odor of tar, but retained its original characteristic odor. " The formation of tar from olefiant gas begins, therefore, at a temperature which is at any rate higher than 360°, and it appears not to take place below red heat. At a dark red heat, however, the tar is formed in such an amount that it collects in drops." As to the nature of these liquid products little is said, except that they are only partially volatile, carbon always remaining behind. They are not always of the same character, being darker or lighter in color according to the temperature of formation. When the liquids are formed the volume of the gas is diminished. The residual gas consisted for the greater part of marsh gas, but contained also undecomposed ethylene, the vapors of tar and hydrogen. The proportions varied in different experiments. It was shown by Berthelot[2] that the liquid product obtained by heating ethylene is not a single substance, but a mixture of several liquids; among them benzene, styrene and other liquids with higher boiling-points. He found a trace of acetylene in the gaseous residue, and claimed that a large proportion of ethane was formed, and on this basis supposed that the decomposition of ethylene by heat consists in a splitting of two molecules of ethylene into acetylene and ethane, and that the formation of liquid products is due to a subsequent condensation of the acetylene to more complex products. But there is no experimental ground for believing that this sequence is followed in the decomposition, and a careful study of the condition in which Berthelot leaves the matter does not make it clear that he has added materially to the knowledge of the action of heat upon ethylene by these reactions, as it will be observed that starting with almost any hydrocarbon a mixture of compounds can be obtained so complicated as to admit of many explanations. Berthelot's results are also different from those of previous observers, in that he finds ethane as an important decomposition product at red heat where others found marsh gas. The impression conveyed by his work that ethylene is a comparatively stable substance at 600°–700° is not in accordance with other observers.

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[1] Philosophical Magazine, 3d series, **31**, 20, 91, 96.

[2] Journal für praktische Chemie **26**, 478.

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[1] Poggendorff's Annalen der Physik **90**, 1.

[2] Annales de Chimie et de Physique, 4th series, **16**, 144.

Summing up the literature of the subject, it seems that at the highest temperatures ethylene separates directly into its elements. Below this point marsh gas and carbon are obtained, then marsh gas and several liquid products, among them benzene, styrene, etc., under certain conditions. It has also been stated by v. Wilde[1] that under the influence of a silent electrical discharge liquid products are formed in a manner somewhat analogous to the reaction by heat. It has been the endeavor of the present work to extend this knowledge in the direction of lower temperatures.

The fact that a difference is noticed in the action of heat at various temperatures leads to the questions, What is the lowest point at which heat affects the constitution of ethylene? and, What is the nature of the change at that temperature? In order to answer either of these questions, or others which easily present themselves, two conditions must be filled: 1. the gas must be heated at fixed temperatures; 2. the temperatures must be kept constant within the limits in which change is noticed until all change ceases.

In order to fill the last condition a tube of Bohemian glass thirty inches long was cleaned and dried as if for a combustion; both ends were drawn out for eight inches, the small ends were bent at a right angle and each connected by a rubber stopper with a glass cylinder, which could be filled with mercury through a tubulus near the bottom. A small glass tube passing through a second hole in the rubber stoppers served as an exit or entrance tube for air or ethylene. After filling both cylinders with mercury the air in the combustion tube was displaced by ethylene and one cylinder also filled with this gas. The small conducting tubes were then closed. The ethylene could now be passed from one cylinder through the heating tube into the other cylinder by drawing off mercury from one and filling the other. Reversing this process the gas could be forced back through the heated space into the first receiver. Thus the same gas could be subjected to the heat repeatedly until no further change was noticed. By means of this apparatus the general phenomena of the action of heat upon ethylene were studied, at first with little regard to controlling the temperature exactly.

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[1] Berichte der deutschen chemischen Gesellschaft 7, 357.

The ethylene used in all the experiments was prepared by Wöhler's method of heating alcohol and sulphuric acid in the proportion of four parts by weight of sulphuric acid to one part of alcohol, sand being added to prevent foaming. The method gave satisfactory results when only the first half of the gas was used which a given amount of alcohol was capable of yielding. Purification through a Wolff's flask containing strong sulphuric acid and two bottles of caustic soda solution proved insufficient, for the gas still contained sulphur dioxide and moisture. It was therefore purified by passage through concentrated sulphuric acid, caustic soda (four flasks), concentrated sulphuric acid (three flasks), solid caustic potassa, solid calcium chloride, and finally through a tube containing phosphorus pentoxide. This method of purification was used in all the experiments to be described; no sulphur dioxide was found in ethylene thus purified, though tests were made for it repeatedly. It was necessary to pass ethylene through the apparatus for some time before all the air was driven out.

First Series of Experiments.

Ethylene was heated for several hours in the apparatus described, at first without any attempt to determine the temperature, except by noticing that the glass softened slightly. By this means a general idea of the decomposition was obtained. It took place readily. There was blackening in the hottest part of the tube, while in the cooler parts drops of a yellow liquid condensed, and crystalline flakes resembling naphthalene were noticed. On opening the tube an odor similar to naphthalene was very evident. In a second experiment it was noticed that the drops of liquid were at first colorless, but gave a gradation in color through yellow and brown to black in the hottest part of the tube, after the heating had been continued some time. On cooling it was found that the gas had decreased in volume. The residual gas was not analysed, for diffusion had taken place through the rubber stoppers. 5 per cent. of the gas could still be absorbed by sulphuric acid.

It was supposed that all the experiments would be made at temperatures above that of boiling mercury, and a Siemens pyrometer, depending upon the increased resistance of a platinum wire when heated, was used for determining temperature. The pyrometer consisted of a fine platinum wire placed in the tube to be heated; this was welded to thick platinum wires leading to the cool portion of the tube and dipping into the mercury in the reservoirs. The mercury was made part of an electric circuit including a resistance-box and Wheatstone's bridge. The resistance of the whole system was determined for a definite temperature, and the resistance at 0° C. calculated by Siemens' formula,

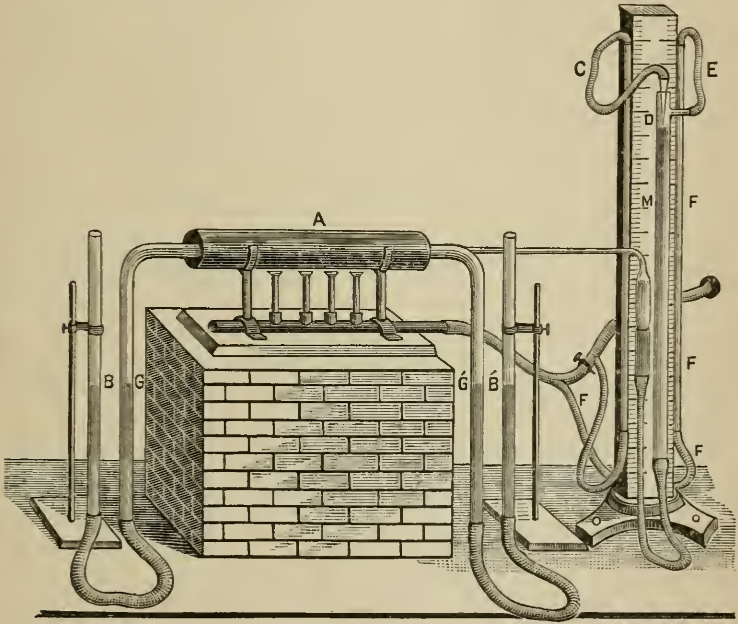
$$R_t = R_o (0.00216407\,T + 0.039369\sqrt{T} - 0.24127),$$

where R_o = the resistance at 0° C., R_t = the resistance at the temperature of the observation, t, and $T = t + 273°$ C. By this means it was determined that the phenomena described above can be observed at a temperature 440° C., from the following data:

$R_o = 1.282$ Siemens' units.
$R_t = 1.956$ " "

The gas used in these experiments was analysed by Hempel's absorption methods, and found to contain 96.6 per cent. ethylene as the mean of four determinations. The remaining 3.4 consisted of air.

In order next to determine the minimum temperature at which ethylene is decomposed, it was heated at a temperature varying from 350° to 375° for five hours. Slight decomposition was evident, for the gas contracted slightly, and its odor was changed altogether, being like that of impure kerosene. As the decomposition was evidently slow at this temperature, and a number of hours would be necessary for each experiment, a careful examination was made to see if the gas could be kept in the heating apparatus absolutely without leakage. It was filled with ethylene, and a portion drawn off and analysed by absorption; the apparatus, which was apparently air-tight, was then allowed to stand for about twenty-four hours, and the gas then analysed again, from which it was seen that air had diffused through the rubber joints. After trying various devices it became evident that ethylene could not be kept in such an apparatus for the length of time required for an experiment of this kind without diffusion through the rubber. It was necessary, therefore, to arrange the apparatus without rubber joints, and for greater security, joints of all kinds were made unnecessary by the following arrangement (see Figure).



A tube of moderately hard glass about five feet long was bent twice at right angles, and the ends drawn out so as to allow rubber tubes to slip over them. These rubber tubes were connected with two open glass tubes, *B* and *B'*. Ethylene was passed through *B* until all the air was expelled from the whole apparatus; mercury was then poured into *B* and *B'* so that the gas was confined over mercury alone. By raising or lowering *B* or *B'*, the pressure could be adjusted to that of the atmosphere, and any change in volume could be noticed at once by a change of the mercury level. The portion of the tube to be heated was enclosed in a cylindrical air-bath of sheet iron, *A*. This was heated by a small gas furnace. Low temperatures were determined by a mercury thermometer; but as this could not be used for temperatures above 300°, and as it was impracticable to use the Siemens pyrometer in this apparatus, an air-thermometer of the form devised by Joly[1] was arranged with a specially constructed air bulb about eight inches long and one inch inner diameter; this was placed close beside the heating tube and both packed in asbestos.

In order to maintain constant temperature the following gas regulator was devised, and gave satisfactory results. A branch pipe *c*, from the gas-supply passed to the top of the air-thermometer and terminated in a fine glass jet, *d*, which dipped under the mercury in the manometer which indicates the pressure of the air-thermometer. The top of the manometer was then enclosed by a glass tube, so as to convey the gas by the tube *f* to the furnace. If the temperature of the thermometer bulb was lowered slightly, the mercury in the manometer sank and opened the jet from the branch tube *c*, sending an additional supply of gas to the furnace; by this means the temperature was raised again, until the branch supply was cut off by the rising mercury.

Ethylene, which by absorption analysis was 99.6 per cent. pure, was heated in this apparatus for seven and a half hours at 250°. On cooling the gas returned to its original volume, and there was no sign of change in constitution. The temperature was then raised to 275° and kept as near that point as possible for seven hours, and again no change in constitution was noticed. The same gas was then heated to 300° for fourteen hours with the same result. It had been noticed repeatedly before that on heating ethylene to 350° to 375° a marked change in odor accompanied the decomposition; this was not noticed in the gas heated to 300°, the odor remained that of pure ethylene. As a final proof that no change in constitution had taken place, the gas before and after heating was analysed by combustion.

Analysis of Ethylene Before Heating.

	Volume.	Press.	Temperature.	Volume reduced to 1 meter and 0°.
Volume taken for analysis,	73.2	.1372	22.0	9.29
Volume after adding air,	383.3	.4454	22.0	158.00
Volume after explosion,	367.4	.4094	22.5	139.00
Volume after absorption of CO_2,	345.7	.3801	25.0	120.40

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[1] Poggendorff's Annalen der Physik und Chemie, Jubelband, 82.

Theoret. volume of CO_2 = 9.29 × 2 = 18.58 vols.
Found volume of CO_2 = 18.60
Theoret. volume of water vapor = 18.58
Found volume of water vapor = 18.00

Analysis of Ethylene After Heating.

	Volume.	Press.	Temperature.	Volume reduced to 1 meter and 0°.
Volume taken for analysis,	70.1	.1451	20.0	9.48
Volume after adding air,	470.8	.5432	20.7	238.3
Volume after explosion,	461.5	.5132	22.0	219.2
Volume after absorption of CO_2,	440.8	.4878	21.2	199.7

Theoret. volume of CO_2 = 18.96 vols.
Found volume of CO_2 = 19.7
Theoret. volume of water vapor = 18.96
Found volume of water vapor = 19.10

The two analyses agree sufficiently to show that no change was effected by the heating.

Second Series of Experiments.

Ethylene was passed through the heating tube until an absorption analysis showed it to contain ethylene more than 99 per cent. pure. The volume occupied by the gas was then marked off on the tube and the temperature of the room noted by the air-thermometer. The air-bath was then raised to 317° and kept between 315° and 320° for five hours. On cooling no change in volume was noticed. The heating was continued at 328°, 338°, 344°, successively for several hours with the same result. A very slight contraction was noticed at the last temperature, but it was not observed again, and was probably due to a rise in temperature beyond 344°. The gas was then kept at 350° to 355° for eight hours; on cooling slight contraction in volume was evident. By heating for sixteen hours longer the contraction approximated one-twentieth of the whole gas. It amounted to seven cubic centimeters in all, and hence could be easily observed. On heating the gas further at this temperature no more contraction could be obtained. The gas now had the sharp, disagreeable odor noticed before. It was all absorbed by fuming sulphuric acid. No permanent gas, such as methane or hydrogen, remained. It is evident that the condensation must have resulted from polymerisation of ethylene. It will be observed that a condensation of two or more molecules of a hydrocarbon of the ethylene series will yield a hydrocarbon of the same series. If, on the other hand, a hydrocarbon of any other series had been formed, then hydrogen or a saturated hydrocarbon must have been formed which would not have been absorbed by sulphuric acid. The change in the gas was so slight that it did not affect the results of a combustion analysis of the gas.

Ethylene which had been heated at 350° until no further change could be noticed was then heated to 358° for eight hours without further contraction. On heating at 375° contraction began again, and continued until the whole volume was reduced by one-fifteenth —*i. e.*, 150 cc. were reduced to 140 cc. The gas was still all absorbed by fuming sulphuric acid. On heating to 400° and maintaining the temperature between 400° and 408° for five hours, contraction continued slowly. As the contraction did not stop, the heating was continued for 171 hours, the last 70 hours being uninterrupted. The total change in volume was from 132 cc. to 63 cc. The gas did not contract further at 400°. During the first days of the heating a small trace of some liquid substance appeared in the cool part of the tube. It was colorless at first, but became brown as it increased in quantity, finally amounting to two or three drops. A qualitative examination of the residual gas showed that a part was absorbed by ordinary strong sulphuric acid. The remaining part was not absorbed even by fuming sulphuric acid. Thus no ethylene remained undecomposed.

Analysis of Residual Gas.

	Volume.	Press.	Temp.	Volume reduced to 1 meter and 0° C.
Volume of gas taken	253.2	.3059	7.0	75.5
Volume of gas after adding air	371.3	.4210	2.5	154.9
Volume of gas after absorption with H_2SO_4,	346.5	.4110	7.5	139.3
Volume of gas taken for combustion	289.0	.3695	14.0	101.5
Volume of gas after adding oxygen	452.2	.5055	12.0	219.1
Volume of gas after explosion	344.5	.4117	13.2	135.3
Volume of gas after absorption of CO_2	261.3	.3309	11.5	82.9
Volume of gas after adding hydrogen.	329.1	.3915	10.5	124.1
Volume of gas after explosion	216.7	.2946	10.5	61.5
Volume of gas after adding hydrogen	301.3	.3632	12.5	104.6
Volume of gas after explosion	255.2	.3287	12.5	80.2

Contraction = 136.2
CO_2 = 52.4
Nitrogen = 53.9

Since only part of the gas was taken for combustion, the volumes found must be multiplied by $\frac{139.3}{101.5}$ to correspond to the whole volume of gas which gives

Contraction = 192.8
CO_2 = 71.9
Nitrogen = 74.0

In transferring the original gas from the heating tube to the eudiometer 12.8 volumes of air were introduced, which subtracted from the total volume leave 62.7 volumes of the mixture of hydrocarbons to be considered in the analysis.

Volume of gas taken = 75.5
Air in above gas = 12.8
Mixture of hydrocarbons = 62.7
Hydrocarbons absorbed by H_2SO_4 = 15.6
47.1
Carbon dioxide obtained = 71.9
Contraction = 186.9

The volume of carbon dioxide is more than would have been produced by marsh gas and less than ethane would have furnished. It can represent a mixture of ethane with marsh gas or with hydrogen. By passing the gas over spongy palladium under the conditions recommended by Hempel it was shown that no hydrogen was present; the gas therefore seemed to be a mixture of 22.3 volumes methane and 24.8 volumes ethane.[1] The entire gas seemed to be composed, therefore, of

Hydrocarbons of C_nH_{2n} series, ...	15.6 vols.
Ethane, ...	24.8
Methane, ...	22.3
	62.7

The liquid formed during the heating combined very readily with bromine without any noticeable evolution of hydrobromic acid. The amount was too small for any further investigation except to show by Hofmann's[2] test that benzene was absent.

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[1] Bunsen's gasometrische Methoden, p. 62.

[2] Annales de Chimie et de Physique, 2d series, **43.**

Ethylene was next heated for 102 consecutive hours at 450°. The contraction proceeded more rapidly than at 400°. After seventy-two hours the contraction ceased, and the volume remained constant for thirty hours. The original volume, 150 cc., was reduced to 84.2 cc. The liquid had the same characteristics as before; the tube was very slightly blackened.

Analysis of Residual Gas.

	Volume.	Press.	Temp.	Volume reduced to 1 meter and 0°C.
Volume of gas taken	250.8	.3114	12.0°	74.87
Volume after absorption with ordinary H_2SO_4	217.5	.2849	11.5	59.50
Volume after absorption with fuming H_2SO_4	217.5	.2849	11.5	59.50
Volume after adding oxygen	320.3	.3875	12.0	118.9
Volume after explosion	391.2	.4458	13.0	166.5
Volume after adding oxygen	578.9	.6325	16.0	347.7
Volume after explosion	401.1	.4549	16.0	172.4
Volume after absorption with KOH	287.7	.3564	17.0	96.5

Air was introduced in transferring from the heating apparatus to the eudiometer; its amount was determined by an independent analysis to be 19.2 volumes.

Original volume = 74.87
Air = 19.2

Mixture of hydrocarbons, = 55.67
Hydrocarbons of C_nH_{2n} series = 15.37

Mixture of methane and ethane = 40.30

As in the former analysis it was shown that this mixture consisted of 35.6 volumes ethane and 4.7 volumes methane, or the whole residual gas contained

Hydrocarbons of C_nH_{2n} series, . . .	15.37
Ethane, ...	35.6
Marsh gas, ...	4.7
	55.67

The effort was made to heat ethylene at 500°, but the air-thermometer bulb softened at this temperature. It was evident that the decomposition was different at this temperature, for the tube was blackened by a considerable deposit of charcoal.

The facts which this work has established are, 1. Ethylene undergoes change by the action of heat at a temperature very much lower than has been observed in previous investigations. 2. The temperature at which ethylene begins to alter in constitution is about 350°C. 3. The change at this temperature consists in condensation without the formation of members of any series of hydrocarbons having a different percentage of carbon and hydrogen from ethylene. The change is slow, requiring at least twenty hours before it ceases, and it is not then complete. 4. If ethylene is heated to 400° for a sufficient length of time it is entirely decomposed with formation of marsh gas, ethane and liquid products, which will be investigated further.

Chemical Laboratory, Johns Hopkins University.

PARA-NITRO-BENZOIC SULPHINIDE.

By W. A. Noyes.

In the study of the oxidation of benzene derivatives with potassium ferricyanide I wished to include an ortho-sulphamide. The ease with which para-nitro-toluene is oxidised by the agent in question, and the fact that when treated with fuming sulphuric acid it readily yields an acid containing the sulphonic group ortho to the methyl, suggested the corresponding sulphamide as likely to be well suited for my purpose. As this sulphamide had never been oxidised, it was thought best to study first the product obtained by oxidising it with potassium permanganate. The sulphinide obtained has proved to be of rather unusual interest, and, together with the corresponding amido-sulphinide, throws considerable light upon the character of the sulphinides.

As Remsen[1] proposes to make a thorough study of the sulphinides, I will not discuss the bearing of the facts which I have discovered, but will simply state that they furnish a strong confirmation of the opinion expressed by Remsen[1] that the more common and perhaps the only form of the salts of the sulphinides is $R\mathord{<}\substack{CO \\ SO_2}\mathord{>}NM$, and not, as was at first supposed, $R\mathord{<}\substack{CO_2M \\ SO_2NH_2}$. An examination of the analytical data for the salts of other sulphinides obtained by Remsen and his co-workers makes it seem probable that some of these, at least, were also of the first form, and not of the last.

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[1] This Journal **6**, 260. The experiments here described were partly completed before that paper was published. In a letter to Professor Remsen, written in April of that year, I mentioned some of the results which I had obtained, and in his reply I first learned that he was engaged in an extended study of the sulphinides. He kindly informed me that the study of the sulphinide which I was working with should not be taken up in his laboratory.

Preparation of Para-nitro-ortho-toluene-sulphamide.

Para-nitro-ortho-sulpho-toluene was obtained essentially as described by Hart.[2] Fifty grams of para-nitro-toluene were put in a flask, and 200 grams of a strongly fuming sulphuric acid were added. The mixture grew warm spontaneously, and in a few minutes a solution was obtained from which no nitro-toluene was precipitated on pouring it into water. The whole was then poured into water, neutralised with chalk, and the filtrate from the precipitated calcium sulphate was evaporated to dryness, and the calcium salt obtained was dried at 150°.

It was found that merely triturating the calcium salt with phosphorous pentachloride, or even heating the two together in a porcelain dish, converted but a small portion into the sulphochloride. Accordingly, the calcium salt and an equal weight of the pentachloride were intimately mixed and put in a flask. The mixture was then heated by immersing the flask in a boiling water-bath for twelve hours. At the end of the time all lumps of the pentachloride had disappeared, and the contents of the flask had the consistency of thick cream. The contents of the flask were poured into water, and the sulphochloride, which, under these circumstances, was liquid and did not solidify on cooling, was separated from the acid solution with a separatory funnel. It was then converted into the sulphamide by warming with concentrated aqueous ammonia. The sulphamide was easily purified by boiling with bone-black and crystallising from hot water. The amide crystallises in fine needles, which usually have a slight yellow color, but which may be obtained perfectly white. It fuses at 186°–187° (uncor.).

The potassium salt of para-nitro-ortho-sulpho-toluene was also prepared, and as I find no recorded analysis, I will give mine, and also a solubility determination. The analysis was as follows:

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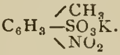
[1] This Journal **6**, 262.

[2] *Ibid.* **1**, 350.

0.3701 gram of the salt gave 0.1236 gram K_2SO_4.

	Calculated for  $C_6H_3\begin{array}{l} \diagup CH_3 \\ -SO_3K. \\ \diagdown NO_2 \end{array}$	Found.
K	15.29	14.97

6.29 grams of a solution saturated at 16° left on evaporation 0.1606 gram of the salt dried at 150°. Victor Meyer's method.

100 parts of water at 16° dissolve 2.62 parts of the salt.

Oxidation of Nitro-toluene-sulphamide.

Several experiments were tried for the purpose of finding the best conditions for oxidation. The following method was found to be the most satisfactory: 5 grams of the amide were put in a flask with 500 cc. of water, 1 gram of potassium hydroxide was added, and then 10 grams of potassium permanganate in separate portions, while the whole was heated by immersion in a boiling water-bath. The amide is not entirely oxidised by the ten grams of permanganate, but if more is added it seems to act fully as much on the product of oxidation as on the amide, and the yield of the former is scarcely increased. After the permanganate was completely reduced the solution was filtered from the oxide of manganese, and the filtrate was nearly neutralised or rendered slightly acid with sulphuric acid. This usually caused the separation of about two grams of the unoxidised amide, which was filtered off and used for a new oxidation. The chief object of the neutralisation was to prevent a decomposition which seemed to take place when the alkaline solution was evaporated. On evaporating the neutral solution, filtered from the precipitated amide, to a small bulk and allowing it to cool, a difficultly soluble salt separated, which proved to be *potassium anhydro-nitro-sulphamine-benzoate*. The same salt may be obtained when the oxidation is conducted without the addition of potassium hydroxide, but the yield is very much smaller. The salt was purified by boiling repeatedly with alcohol to remove some of the amide with which it was always mixed, and by recrystallising from water.

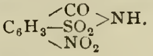
Para-nitro-benzoic Sulphinide.

When hydrochloric acid is added to a hot, concentrated solution of the potassium salt, para-nitro-benzoic sulphinide separates from the solution on cooling. Under these circumstances the sulphinide crystallises sometimes in small leaflets and sometimes in fine needles. Both fuse at 209° (cor.). On spontaneous evaporation of its solutions it crystallises in short, thick prisms which combine together in macles. It is difficultly soluble in cold water, though scarcely less soluble than its potassium salt. It is more easily soluble in hot water, rather difficultly soluble in alcohol, and only slightly soluble in ether. The sulphinide and its salts have an intensely bitter taste, reminding one of quinine. Benzoic sulphinide, it may be remembered, is remarkably sweet.[1] The amido-sulphinide to be described below is also very sweet. The analyses were made with two different specimens with the following results:

I. 0.1150 gram gave 0.1212 gram $BaSO_4$ (Liebig's method as modified by Keiser[2]).

II. 0.1439 gram gave 0.1468 gram $BaSO_4$ (Carius).

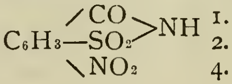
III. 0.1412 gram gave 0.1437 gram $BaSO_4$ (Carius).



$C_6H_3\begin{array}{l}\diagup CO \\ -SO_2 \\ \diagdown NO_2\end{array}\!>NH.$

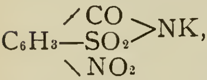
	Calculated for $C_6H_3\begin{array}{l}\diagup CO \\ -SO_2 \\ \diagdown NO_2\end{array}\!>NH.$	Found.		
		I.	II.	III.
S	14.04	14.47	14.02	13.99

From the method of preparation para-nitro-benzoic sulphinide must have the structure



$C_6H_3\begin{array}{l}\diagup CO \\ -SO_2 \\ \diagdown NO_2\end{array}\!>NH \quad \begin{array}{l}1. \\ 2. \\ 4.\end{array}$

Potassium Anhydro-nitro-sulphamine-benzoate,



$C_6H_3\begin{array}{l}\diagup CO \\ -SO_2 \\ \diagdown NO_2\end{array}\!>NK,$ prepared as described above, crystallises from a hot solution in fine leaflets. The salt is easily soluble in warm water, but difficultly soluble in cold. In order to establish the composition of the salt beyond question, determinations of potassium, hydrogen and sulphur were made. The results were as follows:

I. 0.1568 gram of the salt gave 0.0507 gram K_2SO_4.

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[1] This Journal **1**, 430.

[2] *Ibid.* **5**, 207.

II. 0.1866 gram of the salt gave 0.0606 gram K_2SO_4.

III. 0.3591 gram of the salt, burned with copper oxide, gave 0.0422 gram H_2O.

IV. 0.3443 gram of the salt gave, in the same way, 0.0403 gram H_2O.

V. 0.1387 gram of the salt gave 0.1187 gram $BaSO_4$ (Liebig).

VI. 0.1836 gram of the salt gave 0.1629 gram $BaSO_4$ (Liebig).

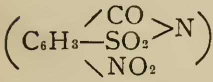
	Calculated for $C_6H_3\begin{array}{l}\diagup CO \\ -SO_2 \\ \diagdown NO_2\end{array}\!\!>NK.$	Found.						Calculated for $C_6H_3\begin{array}{l}\diagup CO_2K \\ -SO_2NH_2. \\ \diagdown NO_2\end{array}$
		I.	II.	III.	IV.	V.	VI.	
K	14.66	14.50	14.56	...	...	...	...	13.73
H	1.13	...	...	1.31	1.30	...	...	1.76
S	12.03	...	...	...	...	11.75	12.18	11.27

A solubility determination was made with the following results:

8.83 grams of a solution saturated at 18.5° left on evaporation 0.0836 gram of the salt.

100 parts of water at 18.5° dissolve 0.96 part of the salt.

Barium Anhydro-nitro-sulphamine-benzoate,



$\left(C_6H_3\begin{array}{l}\diagup CO \\ -SO_2 \\ \diagdown NO_2\end{array}\!\!>N\right)_2Ba + 3H_2O$. This was obtained by boiling the nitro-sulphinide with barium carbonate and water. The solution of the salt was filtered from the excess of barium carbonate, evaporated somewhat and allowed to cool, when the salt separated in well-formed, short prisms which had a tendency to a concentric grouping. The salt has a bitter taste. The analyses were as follows:

I. 0.3783 gram of the salt lost 0.0322 gram H_2O at 145°.

II. 0.3361 gram of the salt lost 0.0288 gram H_2O at 145°.

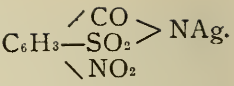
	Calculated for $\left(C_6H_3\begin{array}{l}\diagup CO \\ -SO_2 \\ \diagdown NO_2\end{array}\!\!>N\right)_2Ba + 3H_2O.$	Found.	
		I.	II.
H_2O	8.37	8.51	8.57

The salt can be heated to 210° without decomposition.

I. 0.2835 gram of the anhydrous salt gave 0.1117 gram $BaSO_4$.

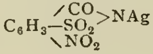
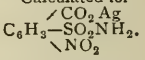
II. 0.3073 gram of the anhydrous salt gave 0.1211 gram $BaSO_4$.

	Calculated for $\left(C_6H_3\begin{array}{l}\diagup CO \\ -SO_2 \\ \diagdown NO_2\end{array}\!\!>N\right)_2Ba.$	Found.		Calculated for $\left(C_6H_3\begin{array}{l}\diagup CO_2 \\ -SO_2NH_2 \\ \diagdown NO_2\end{array}\right)_2Ba.$
		I.	II.	
Ba	23.18	23.17	23.18	21.85

Silver Anhydro-nitro-sulphamine-benzoate, 
$C_6H_3\left\{\begin{matrix}\left.\begin{matrix}CO\\SO_2\end{matrix}\right\rangle NAg\\NO_2\end{matrix}\right.$

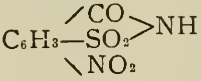
The silver salt of the sulphinide was prepared by precipitating a solution of the potassium salt with silver nitrate. The precipitated salt was washed thoroughly with cold water and dried by allowing it to stand for some time loosely covered with filter paper. It is almost insoluble even in boiling water. The salt contains no water of crystallisation. The analyses were as follows:

I. 0.1291 gram of the salt gave 0.0413 gram Ag.
II. 0.1549 gram of the salt gave 0.0498 gram Ag.
III. 0.2086 gram of the salt gave 0.0673 gram Ag.

	Calculated for  $C_6H_3\left\{\begin{matrix}\left.\begin{matrix}CO\\SO_2\end{matrix}\right\rangle NAg\\NO_2\end{matrix}\right.$	Found.			Calculated for  $C_6H_3\left\{\begin{matrix}CO_2Ag\\SO_2NH_2.\\NO_2\end{matrix}\right.$
		I.	II.	III.	
Ag	32.24	31.99	32.15	32.26	30.59

Para-amido-benzoic Sulphinide.

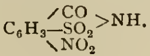
Six grams of the potassium salt of the nitro-sulphinide were placed in a flask, and 15–20 cc. of concentrated ammonia were added. A rapid current of hydrogen sulphide was then passed into the mixture. Solution took place speedily with a considerable evolution of heat. The current of gas was continued for a few minutes longer, and the solution was then poured into a porcelain dish and evaporated to dryness on the water-bath. The residue was treated with water and filtered to remove the sulphur which had separated. On acidifying the filtrate with hydrochloric acid, para-amido-benzoic sulphinide separated mixed with some sulphur. It was purified by crystallising from water.

Para-amido-benzoic sulphinide, 
$C_6H_3\left\{\begin{matrix}\left.\begin{matrix}CO\\SO_2\end{matrix}\right\rangle NH\\NO_2\end{matrix}\right.$ 1, 2, 4, crystallises in fine needles, which usually have a slight yellow color. The color can be removed, however, by dissolving the substance in alcohol and pouring the solution into water. The sulphinide is almost insoluble in cold water, difficultly soluble in hot water, rather difficultly soluble in alcohol and ether. Its solution, even when very dilute, shows a beautiful dark blue fluorescence. It has an intensely sweet taste. When heated rapidly it fuses at 283°–285° (cor.), and immediately decomposes.

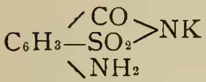
The portion used for the first analysis was obtained by crystallising once from hot water as described above. That used for the second analysis was obtained by acidifying a solution of the barium salt with hydrochloric acid and washing the precipitated sulphinide thoroughly with water. The results were as follows:

I. 0.1188 gram gave 0.1416 gram $BaSO_4$ (Carius).

II. 0.1470 gram gave 0.1735 gram $BaSO_4$ (Carius).

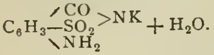
	Calculated for  $C_6H_3\begin{matrix}\diagup CO\\ -SO_2\\ \diagdown NO_2\end{matrix}\!>NH.$	Found.	
		I.	II.
S	16.16	16.37	16.20

Potassium Anhydro-amido-sulphamine-benzoate,



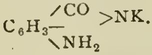
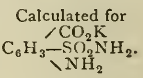
$C_6H_3\begin{matrix}\diagup CO\\ -SO_2\\ \diagdown NH_2\end{matrix}\!>NK + H_2O.$ A weighed portion of the amido-sulphinide was neutralised with the calculated amount of a standard solution of potassium hydroxide. The salt proved to be very easily soluble in water. On allowing the solution to evaporate spontaneously the salt was deposited on the sides of the beaker in a crust creeping nearly to the top. Under a glass the crust was seen to consist of fine needles. Portions of this crust lost water rapidly on standing over calcium chloride and became effloresced in appearance. The amount of water lost indicates that the salt prepared as described above contains eight molecules of water and loses seven molecules on standing over calcium chloride. Two determinations of the water lost over calcium chloride gave respectively 32.47 and 34.23 per cent. Theory requires for a salt containing eight molecules of water and losing seven, 33.16 per cent. Not much reliance is placed on the analyses, as there was not sufficient evidence of the purity of the salt. The salt is soluble with difficulty in cold alcohol of 90 per cent., but more easily soluble in hot alcohol. From the hot solution it separates, on cooling, in long, well-formed, fine needles, which contain one molecule of water. They are, however, hygroscopic, and retain, even while standing over calcium chloride, a small portion of hygroscopic moisture, so that the determinations of water do not agree well with the calculated amount. The same remark applies to the salt at first described. The first analysis given below was with the salt obtained by spontaneous evaporation of the aqueous solution. The other two analyses were with the salt crystallised from alcohol. Each salt was dried over calcium chloride.

I. 0.1044 gram of the salt lost 0.0088 gram H_2O at 140°.
II. 0.2447 gram of the salt lost 0.0211 gram H_2O at 140°.
III. 0.1351 gram of the salt lost 0.0109 gram H_2O at 150°.

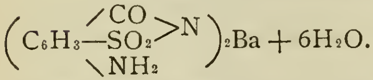
	Calculated for  $C_6H_3\begin{array}{l}/CO\\ -SO_2\\ \backslash NH_2\end{array}>NK + H_2O.$	Found. I.	II.	III.
H_2O	7.09	8.43	8.62	8.07

A portion of the salt which lost 8.30 per cent. of water at 150° regained a little *more* than it had lost on standing open in the laboratory over night. On heating for a half hour at 220° the salt turned slightly brown, but lost less than one-half of one per cent. in weight. The determinations of potassium were as follows:

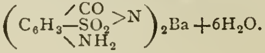
I. 0.0956 gram of the anhydrous salt gave 0.0352 gram K_2SO_4.
II. 0.2236 gram of the anhydrous salt gave 0.0814 gram K_2SO_4.
III. 0.1242 gram of the anhydrous salt gave 0.0450 gram K_2SO_4.

	Calculated for  $C_6H_3\begin{array}{l}/CO\\ -\\ \backslash NH_2\end{array}>NK.$	Found. I.	II.	III.	Calculated for  $C_6H_3\begin{array}{l}/CO_2K\\ -SO_2NH_2.\\ \backslash NH_2\end{array}$
K	16.53	16.50	16.35	16.26	15.35

Barium Anhydro-amido-sulphamine-benzoate,

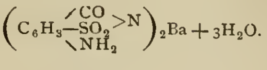

$\left(C_6H_3\begin{array}{l}/CO\\ -SO_2\\ \backslash NH_2\end{array}>N\right)_2Ba + 6H_2O.$ This was obtained by boiling the amido-sulphinide with barium carbonate and a little water. On cooling the solution filtered from the excess of barium carbonate, the salt separated in fine needles. The salt is quite easily soluble in water. It has a sweet taste. Some difficulty was found in determining the water of crystallisation. In warm, dry weather the salt contains a little less water than theory requires for six molecules; in damp weather, on the contrary, the salt contains a little more than the calculated amount. When dried over calcium chloride the salt contains three molecules of water. The analytical results are as follows:

I. 0.3953 gram of the salt lost 0.0369 gram H_2O over $CaCl_2$.
II. 0.3875 gram of the salt lost 0.0358 gram H_2O over $CaCl_2$.

	Calculated for  $\left(C_6H_3\begin{array}{l}/CO\\ -SO_2\\ \backslash NH_2\end{array}>N\right)_2Ba + 6H_2O.$	Found. I.	II.
$3H_2O$	8.45	9.33	9.24

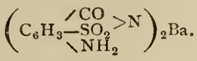
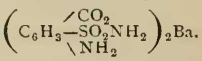
I. 0.3584 gram of the salt dried over $CaCl_2$ lost 0.0330 gram H_2O at 160°.

II. 0.3517 gram of the salt dried over $CaCl_2$ lost 0.0324 gram H_2O at 160°.

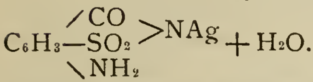
	Calculated for  $\left(C_6H_3\begin{array}{l}/CO\\-SO_2\\ \backslash NH_2\end{array}\!>N\right)_2Ba + 3H_2O.$	Found.	
		I.	II.
$3H_2O$	9.23	9.21	9.21

I. 0.2933 gram of the anhydrous salt gave 0.1282 gram $BaSO_4$.

II. 0.2086 gram of the anhydrous salt gave 0.0910 gram $BaSO_4$.

	Calculated for  $\left(C_6H_3\begin{array}{l}/CO\\-SO_2\\ \backslash NH_2\end{array}\!>N\right)_2Ba.$	Found.		Calculated for  $\left(C_6H_3\begin{array}{l}/CO_2\\-SO_2NH_2\\ \backslash NH_2\end{array}\right)_2Ba.$
		I.	II.	
Ba	25.80	25.67	25.65	24.16

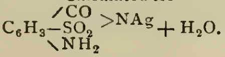
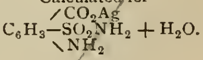
Silver Anhydro-amido-sulphamine-benzoate,


$C_6H_3\begin{array}{l}/CO\\-SO_2\\ \backslash NH_2\end{array}\!>NAg + H_2O.$ When silver nitrate is added to a solution of the barium salt, the silver salt separates as a white, amorphous precipitate. After washing thoroughly with cold water and drying in the air, this contains one molecule of water. The salt loses three-fourths of its water on standing for a day over sulphuric acid. It is soluble with difficulty in hot water, and crystallises from the solution, on cooling, in fine needles, which have a slight brown color. These lost less than one per cent. of water on heating to 170°. Hence the crystallised salt seems to be anhydrous. The analyses given below were with the precipitated, air-dry salt.

I. 0.1884 gram of the salt lost 0.0105 gram H_2O at 160° and gave 0.0622 gram Ag.

II. 0.2050 gram of the salt lost 0.0108 gram H_2O at 160° and gave 0.0690 gram Ag.

III. 0.2086 gram of the salt lost 0.0112 gram H_2O at 160° and gave 0.0702 gram Ag.

	Calculated for  $C_6H_3\begin{array}{l}/CO\\-SO_2\\ \backslash NH_2\end{array}\!>NAg + H_2O.$	Found.			Calculated for  $C_6H_3\begin{array}{l}/CO_2Ag\\-SO_2NH_2\\ \backslash NH_2\end{array} + H_2O.$
		I.	II.	III.	
H_2O	5.56	5.69	5.27	5.37	5.28
Ag	33.45	33.74	33.66	33.65	31.67

An analysis of the crystallised salt, dried at 170°, gave 35.47 per cent. of Ag. Theory requires 35.41 per cent.

UNIVERSITY OF TENNESSEE, *November* 10, 1885.

ON THE OXIDATION OF BENZENE DERIVATIVES WITH POTASSIUM FERRICYANIDE.[1]

By W. A. Noyes.

III.

Remsen and Fahlberg, in studying the oxidation of ortho-toluene-sulphamide with potassium permanganate, discovered the substance known as benzoic sulphinide. By oxidising the same sulphamide with potassium ferricyanide, I have, to my surprise, found that the chief product of the oxidation is not the sulphinide, but ortho-sulphamine-benzoic acid, the acid of which benzoic sulphinide is the anhydride. This is the first *ortho*-sulphamine acid ever prepared, as in all cases heretofore studied, where the oxidising agent has been potassium permanganate, sulphinides have been obtained, and it has seemed probable, for that reason, that a carboxyl-group could not exist in the ortho-position to a sulphamide-group. The experiments here described show that the two groups may exist in the ortho-position to each other, and that the formation of benzoic sulphinide depends, in part at least, upon the oxidising agent used in its preparation.

As much difficulty was experienced in obtaining the ortho-toluene-sulphamide used in the experiments, I will notice briefly the methods which were tried for its preparation. The portion used in the first experiments was prepared, as by Remsen and Fahlberg,[2] from the sulphonic acids obtained by the direct treatment of toluene with fuming sulphuric acid. The process is a very tedious one, and the yield is very poor. An attempt was next made to prepare it from para-nitro-toluene by the method described by Ascher.[3] The purest amide obtained in this way fused at 146°, and it was found impossible to purify it by crystallising it from alcohol or from a mixture of alcohol and ether. Finally, much more satisfactory results were obtained by the process described by Claesson and Wallin.[4]

150 grams of sulphuryl-hydroxyl chloride were put in a flask fitted with a drop-funnel and with a delivery-tube, which was connected with a wide tube that dipped just under the surface of water in a beaker. 60 grams of toluene were added slowly from the

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[1] This Journal **7**, 145. [2] *Ibid.* **1**, 426, and **1**, 170. [3] Annalen **161**, 8. [4] Berichte **12**, 1848.

drop-funnel, while the flask was placed in cold water and shaken constantly to prevent the temperature from rising too much. After the toluene was all added the mixture was poured into cold water. In this way there were obtained directly, from 200 grams of toluene, 236 grams of the crude toluene-sulpho-chlorides. This process entirely avoids the tedious conversion of the sulphonic acids into the sulpho-chlorides through the calcium and potassium salts. The liquid sulpho-chloride was separated as completely as possible from the para-compound by cooling with a freezing mixture, and was then converted into the amide by treatment with aqueous ammonia. The amide was purified essentially as described by Remsen and Fahlberg,[1] except that after boiling several times with water the amide remaining undissolved was treated with chloroform to remove a dark, gummy impurity.

In recrystallising the amide it was found best to treat it with enough boiling water to bring it almost entirely into solution; on cooling the solution to about 70° and keeping it at that temperature for some time, while it is frequently stirred, most of the ortho-amide separates as a granular precipitate, while a mixture of ortho- and para-amides, which cannot be further separated by crystallisation, remains in solution, and can be separated from the ortho-amide by filtering hot. On recrystallising the ortho-amide separated in this way, it is usually perfectly pure. From 200 grams of toluene there were obtained 33 grams of the pure ortho-amide fusing at 155°.

Claesson and Wallin obtained, besides the ortho-toluene-sulphamide, another amide fusing at 108°, which they considered as a meta-compound, although they were familiar with the work by which Fahlberg[2] showed that a similar amide obtained from the sulphonic acids formed, when toluene is treated directly with fuming sulphuric acid, is not meta-toluene-sulphamide, but a mixture of the ortho- and para-amides. As I obtained some of the same amide fusing at 108°–110°, it seemed of interest to determine whether it was in reality a meta-amide or not.

Seven grams of the amide were accordingly boiled for three-quarters of an hour with the usual oxidising mixture of potassium pyrochromate, sulphuric acid and water. Under these conditions both the para[3]- and meta[4]-amide yield the corresponding sulphamine benzoic acids, while the ortho-amide is only slightly attacked. After cooling, the acid formed by the oxidation, together with some unoxidised amide, were filtered off and washed till the filtrate ran through colorless. The acid was then converted into the barium salt by boiling with barium carbonate. The filtrate from the excess of barium carbonate deposited, on cooling, about a gram of an amide which fused at 145°. On dissolving this in hot water and cooling the solution somewhat, an amide separated which fused at 154°; hence, was nearly pure ortho-toluene-sulphamide. The solution of the barium salt was evaporated to dryness, and the residue was treated several times with alcohol to remove the rest of the unoxidised amide. The salt was then recrystallised from water. The salt obtained in this way contained, after drying for three days over sulphuric acid, only 4.33 per cent. of water. The salt of the meta-acid contains, under these circumstances, four molecules of water,[1] which would require 11.82 per cent. The anhydrous salt gave 25.68 per cent. Ba. Theory requires 25.51 per cent. The acid separated from a portion of the crystallised salt fused, and instantly decomposed at 292°–294° (uncor.). The acid separated from the mother-liquors of the salt fused at exactly the same temperature. When heated slowly the acid fused and decomposed at about 280°. Meta-sulphamine-benzoic acid fuses at 246°–247°. (See the following paper.) Hence, the amide fusing at 108°–110° contains both the ortho- and the para-amides, and there is no evidence that it contains anything else. It is undoubtedly the same substance as the amide which was examined by Fahlberg with similar results.

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[1] *Loc. cit.*

[2] This Journal **1**, 172.

[3] Remsen, Annalen **178**, 304.

[4] Remsen and Palmer, this Journal **4**, 142.

Oxidation of Ortho-toluene-sulphamide.

The ortho-toluene-sulphamide was oxidised by boiling it in lots of 3 grams each, with 75 grams of potassium ferricyanide, 30 grams of caustic potash, and 300 cc. of water. The solutions obtained from several oxidations were united and concentrated by evaporation, and most of the potassium ferrocyanide was removed by crystallisation. Enough dilute sulphuric acid was then added to convert all of the potassium carbonate present into the acid carbonate. This precipitated most of the unoxidised amide along with a considerable quantity of potassium sulphate. The filtrate from these was then made strongly acid and extracted with ether. The acid is removed from the solution with some difficulty, and it is necessary for that reason to repeat the extraction many times.

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[1] Remsen and Palmer, *loc. cit.*

The ether was distilled, and the acids which remained were converted into the barium salts in the usual way. The solution was evaporated, and a syrupy residue was treated several times with alcohol to remove any of the unoxidised amide which it contained. The residue was dissolved in hot water and the solution evaporated somewhat. On cooling, a rather difficultly soluble salt was deposited in well-formed, thick needles, which had a strong tendency to a concentric grouping. They were perfectly white in color. In order to insure perfect purity the crystals were air-dried, and then, after pulverising them finely, they were treated several times with ether. The salt was then recrystallised from water as before.

Ortho-sulphamine-benzoic Acid.

Two grams of the salt last mentioned were dissolved in hot water, and the solution was acidified with hydrochloric acid. On cooling, an acid separated in fine needles. In another case, when a mixture of the barium salts of benzoic sulphinide and of ortho-sulphamine-benzoic acid was acidified, the sulphinide separated almost immediately as a granular precipitate, while the acid separated slowly on allowing the solution to stand for several days in a cool room. Under these circumstances the acid was composed of quite large, clear, prismatic crystals which appeared to belong to the monoclinic system. The acid is quite readily soluble in cold water, easily soluble in alcohol and ether. It has a pleasant acid taste, but is not sweet. A little of the alcoholic solution, when evaporated spontaneously on a watch-glass, leaves a syrupy residue. The alcoholic solution of benzoic sulphinide evaporated in the same way leaves a dry residue. The ethereal solutions act in much the same way, but in that case the acid soon begins to crystallise at some point, and solidification then proceeds radially to the edges.

When heated rapidly the acid fuses at 165°–167°. If heated slowly it fuses at 153°–155°, apparently owing to its partial conversion into benzoic sulphinide, for, if it is kept at that temperature for a short time, it becomes solid again, and may then be heated to 210° before it will fuse a second time. The substance in the tube then has the intensely sweet taste which is so characteristic of benzoic sulphinide. Pure benzoic sulphinide fusing at 223°–224° (uncor.) was also obtained by heating a portion of the acid to 180° in an air-bath, and recrystallising from water a dark residue which remained in the crucible. That the change is due to a loss of water of constitution and not of crystallisation, is proved by the fact that the salts of the sulphinide are totally distinct from the salts of the acid. For analysis the acid was dried for a short time at 95°.

I. 0.1191 gram of the acid gave 0.1386 gram $BaSO_4$.
II. 0.1132 gram of the acid gave 0.1310 gram $BaSO_4$.
III. 0.1059 gram of the acid gave 0.00730 gram N.

	Calculated for $C_6H_4<\begin{matrix}COOH\\SO_2NH_2\end{matrix}$.	Found. I.	II.	III.
S	15.92	15.98	15.89	...
N	6.97	...	...	6.89

Barium Ortho-sulphamine-benzoate,

$\left(C_6H_4<\begin{matrix}CO_2\\SO_2NH_2\end{matrix}\right)_2Ba + 9H_2O$. This was prepared and purified as described above. When deposited on cooling a warm solution, the salt has the composition given here. On standing over calcium chloride for a day it loses seven molecules of water. The other two molecules are given off slowly at 111°, and more rapidly at 125°. The anhydrous salt is not sweet, but if it is heated to 130° or above it becomes sweet, owing, apparently, to a partial conversion into the corresponding salt of benzoic sulphinide. The salt of benzoic sulphinide was, for the purpose of comparison, prepared essentially as described by Remsen and Fahlberg,[1] except that greater care was taken to completely remove any of the unoxidised amide which it contained. It was found that the barium salt of the sulphinide is isomeric with the salt of the acid when the latter is dried over calcium chloride, but the two salts are not identical. The salt of the sulphinide is sweet in taste; that of the acid is not. The salt of the acid loses *two* molecules of water at 125°; that of the sulphinide loses *four* molecules at the same temperature, and then has the composition $\left(C_6H_4<\begin{matrix}CO\\SO_2\end{matrix}>N\right)_2Ba$. The analysis of the salt gave 12.66 per cent. H_2O and 23.59 per cent. Ba. Theory requires 12.56 per cent. H_2O and 23.91 per cent. Ba.

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[1] This Journal **1**, 428.

When a solution of pure barium ortho-sulphamine-benzoate is evaporated on the water-bath, it deposits, when very concentrated, a salt which crystallises in well-formed prisms or thick needles, and which contains two molecules of water.

The analyses of the salts were as follows:

I. 0.2990 gram of the salt deposited from the cold solution lost 0.0538 gram H_2O over $CaCl_2$.

II. 0.1654 gram of the same salt lost 0.0279 gram H_2O.

	Calculated for $\left(C_6H_4<\begin{smallmatrix}CO_2\\SO_2NH_2\end{smallmatrix}\right)_2Ba + 9H_2O$.	Found. I.	 II.
$7H_2O$	18.03	17.99	16.87

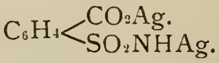
The salt loses its water very easily, and it is probable that the portion used for the second analysis was slightly effloresced, though it had been kept in a corked vial. Analyses I and II following were made with the salt deposited from a cold solution and dried over calcium chloride. Analysis III was made with a salt obtained by evaporating the solution to crystallisation on a water-bath.

I. 0.2452 gram lost 0.0145 gram H_2O at 125° and gave 0.0998 gram $BaSO_4$.

II. 0.1375 gram lost 0.0088 gram H_2O at 125° and gave 0.0557 gram $BaSO_4$.

III. 0.2905 gram gave 0.1185 gram $BaSO_4$.

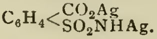
	Calculated for $\left(C_6H_4<\begin{smallmatrix}CO_2\\SO_2NH_2\end{smallmatrix}\right)_2Ba + 2H_2O$.	Found. I.	 II.	 III.
$2H_2O$	6.28	5.91	6.40	...
Ba	23.91	23.94	23.82	23.99

Di-silver Ortho-sulphamine-benzoate, 

$C_6H_4<\begin{smallmatrix}CO_2Ag.\\SO_2NHAg.\end{smallmatrix}$

When silver nitrate is added to a warm solution of the barium salt, a small amount of a salt containing two atoms of silver in the molecule separates at once. If this is filtered off, the slightly acid solution deposits, on cooling, the normal salt containing but one atom of silver in the molecule. The former salt may be obtained in larger quantity by adding to a weighed portion of the acid a little less than twice the amount of ammonia necessary to form the normal ammonium salt. On adding silver nitrate the salt separates as an amorphous precipitate, which becomes crystalline on heating. The salt may be crystallised from hot water, and is then composed of fine leaflets. Both silver salts lose in weight and become sweet in taste on heating to 170°–180°, evidently through a partial conversion into the corresponding salt of the sulphinide. Analysis I was with the salt precipitated from the normal barium salt. The salt for the second analysis was prepared from the barium salt and silver nitrate, with the addition of a little ammonia. The salt was recrystallised from water. The salt for the third analysis was prepared from the acid by adding to it nearly twice the amount of ammonia necessary to form the normal salt, and precipitating with silver nitrate.

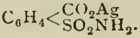
I. 0.0232 gram of the salt gave 0.0121 gram Ag.
II. 0.1063 gram of the salt gave 0.0550 gram Ag.
III. 0.1153 gram of the salt gave 0.0596 gram Ag.

	Calculated for  $C_6H_4<\begin{smallmatrix}CO_2Ag\\SO_2NHAg.\end{smallmatrix}$	Found.		
		I.	II.	III.
Ag	52.05	52.16	51.74	51.69

Mono-silver Ortho-sulphamine-benzoate,

$C_6H_4<\begin{smallmatrix}CO_2Ag\\SO_2NH_2.\end{smallmatrix}$ This is prepared best by adding to the acid a little less than enough ammonia to form the normal salt, and silver nitrate. The salt crystallises in fine, feathery needles. It is much more easily soluble than the di-silver salt. The analyses were made with salts of different preparations.

I. 0.1044 gram of the salt gave 0.0371 gram Ag.
II. 0.0344 gram of the salt gave 0.0119 gram Ag.
III. 0.1024 gram of the salt gave 0.0357 gram Ag.

	Calculated for  $C_6H_4<\begin{smallmatrix}CO_2Ag\\SO_2NH_2.\end{smallmatrix}$	Found.		
		I.	II.	III.
Ag	35.06	35.54	34.59	34.86

Silver Salts of Para-sulphamine-benzoic Acid.

As the silver salts of the sulphamine acids have been little studied, it seemed of interest to see if other salts similar to the first described above could be prepared. At my suggestion Mr. Chas. Walker has prepared and analysed the corresponding salts of para-sulphamine-benzoic acid. The salts were prepared from the ammonium salt essentially as described above. Both salts are very difficultly soluble even in hot water, and they were not recrystallised. The analyses were as follows:

I. 0.2022 gram of the normal salt gave 0.0709 gram Ag.
II. 0.2210 gram of the normal salt gave 0.0774 gram Ag.

	Calculated for $C_6H_4<\begin{matrix}CO_2Ag\\SO_2NH_2\end{matrix}$.	Found.	
		I.	II.
Ag	35.06	35.06	35.02

I. 0.2075 gram of the di-silver salt gave 0.1079 gram Ag.
II. 0.2220 gram of the di-silver salt gave 0.1155 gram Ag.

	Calculated for $C_6H_4<\begin{matrix}CO_2Ag\\SO_2NHAg\end{matrix}$.	Found.	
		I.	II.
Ag	52.05	52.00	52.03

While, so far as I am aware, silver salts of the nature of those last described have never been prepared before, compounds of a similar nature have been known for many years. Thus, Anna Wolkow[1] prepared from para-toluene-sulphamide a potassium salt of the formula $C_6H_4<\begin{matrix}CH_3\\SO_2NHK\end{matrix}$. Gerhardt[2] also refers to silver and mercury salts of similar amides, and shows very clearly in the article referred to that an ammonia residue is either basic or acid in nature, according to the character of the radical or radicals with which it is combined. The effect of an acid radical in giving strong acid properties to an ammonia residue is especially marked in the sulphinides. Strong acids are also formed in some other cases where two of the hydrogen atoms of ammonia are replaced by acid radicals.

The silver salt of benzoic sulphinide was also prepared, for the purpose of comparison, by adding silver nitrate to a solution of its barium salt and crystallising from hot water. It is composed of fine needles, with no tendency to a concentric grouping. It is sweet in taste.

I. 0.1839 gram of the salt gave 0.0683 gram Ag.
II. 0.1139 gram of the salt gave 0.0421 gram Ag.

	Calculated for $C_6H_4<\begin{matrix}CO\\SO_2\end{matrix}>NAg$.	Found.	
		I.	II.
Ag	37.24	37.14	36.97

Remsen and Fahlberg[3] found that when ortho-toluene-sulphamide is oxidised by potassium permanganate, benzoic sulphinide and sulpho-benzoic acid are formed in nearly equal amounts. The same substances are formed, but in comparatively small quantity, when the oxidation is effected by potassium ferricyanide.

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[1] Berichte **3**, 424. [2] Annalen **87**, 298. [3] *Loc. cit.*

After most of the barium ortho-sulphamine-benzoate obtained by boiling the ethereal extract mentioned in the earlier part of this paper with barium carbonate had been crystallised out, the mother-liquors were acidified with hydrochloric acid. A small portion of benzoic sulphinide separated almost immediately as a granular precipitate. On allowing the solution to stand for some time in a cold room a considerable quantity of ortho-sulphamine-benzoic acid separated in quite large, clear crystals. After filtering off, washing and drying, these were easily separated mechanically from the sulphinide. The sulphinide was characterised by its intensely sweet taste, its melting-point of 220°–222° (uncor.), and by its silver salt, which was prepared and analysed. 0.2148 gram of the salt gave 0.0799 gram Ag, which corresponds to 37.19 per cent. Theory requires 37.24 per cent.

For the purpose of determining if any sulpho-benzoic acid was formed by the oxidation, to the solution which had been extracted with ether (see page 179) there was added a solution of ferric sulphate to precipitate the hydro-ferrocyanic acid. The excess of iron in the filtrate from the Prussian blue was precipitated with caustic potash, and to the filtrate from the ferric hydroxide was added enough more caustic potash to expel all ammonia from the solution. After the ammonia was expelled by evaporation, the excess of potassium hydroxide was exactly neutralised with sulphuric acid, the solution was evaporated, and most of the potassium sulphate was removed by crystallisation. The mother-liquors were then evaporated to dryness, and the residue was treated several times with strong alcohol. This seems to have dissolved chiefly potassium ortho-sulphamine-benzoate, and no evidence of the existence of sulpho-benzoic acid in the alcoholic solution could be obtained. The residue insoluble in alcohol was treated several times with a little water, and potassium sulphate was crystallised as far as possible from the solution. Finally the solution was concentrated to about 2 cc., and 3 cc. of strong alcohol were added. The precipitated potassium sulphate was filtered off and the filtrate was evaporated to dryness. The residue was taken up with a very little water, and the solution was acidified with hydrochloric acid. On evaporating over sulphuric acid a few crystals were deposited in clear, well-formed plates. The properties of these agreed, as well as could be judged, with those of the acid potassium salt of ortho-sulpho-benzoic acid as described by Remsen and Fahlberg. The composition was confirmed by analysis. 0.0149 gram of the salt gave 0.0053 gram K_2SO_4, which corresponds to 15.97 per cent. of K. Theory requires 16.25 per cent.

Both benzoic sulphinide and ortho-sulpho-benzoic acid seem to be formed only in very small quantity when the oxidation of ortho-toluene-sulphamide is effected by means of potassium ferricyanide. The chief product of the oxidation is ortho-sulphamine-benzoic acid.

For the purpose of making an approximate estimate of the yield obtained by oxidation, one gram of ortho-toluene-sulphamide was oxidised in the usual manner. After removing most of the potassium ferrocyanide by crystallisation, the unoxidised amide was mostly precipitated by adding enough dilute sulphuric acid to convert the potassium carbonate present into the acid carbonate. The filtrate was then rendered strongly acid and extracted repeatedly with ether. The acids remaining after distilling off the ether were converted into the barium salts, and the barium in these was determined by precipitation as barium sulphate. 0.34 gram of barium sulphate was obtained, which would correspond to 0.59 gram of ortho-sulphamine-benzoic acid. The method given necessarily leaves out of consideration the ortho-sulpho-benzoic acid which is formed, and hence the actual amount of the acids formed must be somewhat greater than the weight given.

One gram of para-toluene-sulphamide treated in essentially the same way gave 0.46 gram of barium sulphate, which corresponds to 0.80 gram of para-sulphamine-benzoic acid. It seems probable from these figures that, as with the nitro-toluenes and the brom-toluenes, the para-amide is a little more easily oxidised than the ortho-compound.

OXIDATION OF META-BROM-TOLUENE.

By W. A. Noyes and Charles Walker.

In the experiments described in a previous paper it has been shown that meta-nitro-toluene conducts itself very differently from either ortho- or para-nitro-toluene when oxidised by potassium ferricyanide. It was of interest, therefore, to study the action of the same agent upon other meta-compounds.

Meta-brom-toluene was prepared from para-acettoluid essentially as described by Grete.[1] 30 grams of para-acettoluid were dissolved in 25 grams of glacial acetic acid and one molecule of bromine was added slowly from a drop-funnel. The brom-acettoluid was precipitated by pouring the solution into water, and was recrystallised from alcohol. The acetyl-group was eliminated by boiling with alcoholic potash, and the brom-toluidine was distilled with water-vapor. It was then dissolved in absolute alcohol and a rapid stream of nitrous acid was passed into the solution. After distilling off the alcohol the meta-brom-toluene was distilled with water-vapor. It was purified by washing with dilute acid and alkali, and finally by distilling again with water-vapor from dilute sulphuric acid.

The oxidation was effected in the usual way by boiling 1 gram of the meta-brom-toluene with 25 grams of potassium ferricyanide, 10 grams of caustic potash and 100 cc. of water. After distilling the unoxidised brom-toluene with water-vapor, filtering, and crystallising out most of the potassium ferrocyanide formed, the solution was acidified and extracted with ether. The residue after distilling the ether was dissolved in a little ether and the solution was evaporated spontaneously. The residues from three oxidations, after drying over sulphuric acid, weighed respectively 0.0121, 0.0112 and 0.0111 gram.

To establish the identity of the acid the residues from several oxidations were boiled with barium carbonate. The barium salt obtained was purified by boiling with bone-black. The acid was then precipitated with dilute hydrochloric acid. It fused at 153.5°.

A comparison with the results obtained in the oxidation of ortho- and para-brom-toluene[2] shows that meta-brom-toluene is a little more easily oxidised than either of those. The amount of the compound oxidised is, however, exceedingly small in each case.

Oxidation of Meta-toluene-sulphamide.

The amide for the oxidation was prepared from pure ortho-brom-toluene. This was prepared from pure ortho-toluidine, partly by the method of Jackson,[3] and partly by that of Sandmeyer.[1] In executing the latter method 12.5 grams of crystallised copper sulphate, 36 grams of potassium bromide, 20 grams of thin sheet copper, 11 grams of concentrated sulphuric acid, and 80 cc. of water were boiled in a flask with an inverted condenser until the reduction to cuprous bromide was complete and the solution became colorless. 10.7 grams of ortho-toluidine were then added, and, after heating nearly to boiling, a solution of 8.8 grams of potassium nitrite in 40 cc. of water was added slowly from a drop-funnel. The ortho-brom-toluene was then distilled from the solution with water-vapor and purified in the usual way. The yield was poor, but about the same as by the method of Jackson. As the previous preparation of hydrobromic acid is avoided, Sandmeyer's method is much easier of execution. Sandmeyer has found the yield poor in the case of other ortho-compounds, and thinks it, possibly, a general law that the reaction does not work smoothly in such cases.

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[1] Annalen **177**, 231.

[2] This Journal **7**, 146.

[3] *Ibid.* **1**, 100.

10 grams of the pure ortho-brom-toluene were converted into the sulphonic acid by dissolving in 30 grams of fuming sulphuric acid. The sodium salt was prepared in the usual way. For the elimination of the bromine a method used by Sandmeyer[2] in a similar case was tried and found to work excellently. The solution of the sodium salt was evaporated to about 200 cc., and 100 cc. of a ten per cent. solution of caustic soda were added. The whole was then boiled gently for two hours with 15 grams of zinc dust. At the end of the time the organic salt in solution was found to be entirely free from bromine. The solution was filtered and nearly neutralised with sulphuric acid, which caused the precipitation of the zinc on boiling for a short time. The filtrate from the zinc hydroxide was evaporated to about 150 cc., and 65 cc. of strong alcohol were added. This caused the separation of most of the sodium sulphate. The filtrate was evaporated to dryness, and the sodium salt of the sulphonic acid was separated still more completely from the sodium sulphate by dissolving it in strong alcohol and filtering. The filtrate was evaporated to dryness, and the residue was treated with an equal weight of phosphorous pentachloride. When the action was complete the mixture was poured into water, and the sulpho-chloride, which fell to the bottom, was separated from the solution by use of a drop-funnel. It was then converted into the sulphamide by treatment with

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[1] Berichte **17**, 2652.

[2] *Ibid.* **18**, 1496.

strong aqueous ammonia. The sulphamide was boiled with bone-black and crystallised from water. It then fused at 90°–91°. Its purity was also established by analysis. 0.1210 gram gave 0.1652 gram $BaSO_4$, which corresponds to 18.74 per cent. of S. Theory requires 18.71 per cent.

The method described above for the elimination of bromine seems to be quite generally applicable, and is much quicker and easier of execution than the method where sodium amalgam is used. The method has also been applied successfully in the preparation of ortho-toluene-sulphamide from para-brom-toluene. It seems probable that potassium hydroxide might be substituted with advantage for sodium hydroxide, as potassium sulphate is much more easily removed from a solution than sodium sulphate.

The oxidation of the meta-toluene-sulphamide was effected in the usual way. The yield was determined as in the oxidation of ortho-toluene-sulphamide (see page 185). Two experiments gave respectively 0.43 and 0.44 gram $BaSO_4$, which correspond to 0.74 and 0.76 gram of meta-sulphamine-benzoic acid. After filtering the barium sulphate the acid in the filtrate was reconverted into the barium salt by boiling with barium carbonate. The salt was purified by evaporating the solution to dryness and treating the residue several times with strong alcohol to remove any of the unoxidised amide which it contained. It was then dissolved in water, the acid was precipitated with hydrochloric acid and recrystallised from hot water. Purified in this way it fused at 246°–247° (uncor.). Palmer[1] gives the fusing-point at 235°. In order to reconcile the discrepancy a small portion of the amide was oxidised with potassium permanganate exactly as described by him. By using the precautions mentioned above to insure purity, an acid was obtained which fused at 246°–247° as before. Palmer's acid was probably contaminated with a trace of the amide which could not be removed by recrystallising from water. The identity of the acid was also established by analysis. 0.1187 gram gave 0.1374 gram of $BaSO_4$, which corresponds to 15.89 per cent. of S. Theory requires 15.92 per cent.

The di-silver salt of the acid was also prepared in the manner described for the ortho- and para-acids. The salt forms an amorphous precipitate, and seems to separate again in the amorphous form when its solution in hot water has cooled. The analyses gave

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[1] This Journal **4**, 144.

51.61 per cent. and 51.50 per cent. Theory requires 52.05 per cent.

There is completed, with the experiments here described, a systematic examination of three classes of toluene derivatives with reference to their conduct when oxidised by potassium ferricyanide in alkaline solution. The results obtained are summarised in the table given below. The numbers indicate the weight in grams of the substituted benzoic acid obtained when one gram of each substance is oxidised with 25 grams of potassium ferricyanide.

Toluene,	0.0090
Ortho-nitro-toluene,	0.69
Meta-nitro-toluene,	0.052
Para-nitro-toluene,	0.73
Ortho-brom-toluene,	0.0044
Meta-brom-toluene,	0.0115
Para-brom-toluene,	0.0065
Ortho-toluene-sulphamide,	0.59 +
Meta-toluene-sulphamide,	0.75
Para-toluene-sulphamide,	0.80

No great accuracy can be claimed for these numbers, of course, and in the case of ortho-toluene-sulphamide the result is known to be too low. However, the results are sufficiently accurate to give an answer to the question which was stated at the beginning of the investigation,[1] so far as toluene derivatives are concerned. Potassium ferricyanide conducts itself in the same manner as potassium permanganate in its ability to oxidise ortho-derivatives. Its conduct in this respect is totally different from that of chromic acid. No support is given, however, to that portion of Richard Meyer's[2] statement of Remsen's law which declares that ortho-groups are more easily oxidised than meta- or para-groups by an alkaline oxidising agent, except in the single case of meta-nitro-toluene. That case seems to be a somewhat anomalous one, and has been discussed in a previous paper. The para-compound seems, in each case, to be oxidised a little more easily than the ortho-compound, but the differences are insignificant.

The difficulty with which the bromine derivatives and toluene itself are oxidised seems to be due, partly at least, to their almost total insolubility. The nitro-toluenes are appreciably soluble in hot water, and for that reason come much more intimately into contact with the oxidising agent. The sulphamides are completely dissolved in the solution which is used for their oxidation, and each of them is quite easily oxidised.

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[1] This Journal **5**, 99.

[2] Aromatische Verbindungen, 179.

Apart from giving a partial answer to the question in consideration of which these investigations were originally commenced, the facts of most interest which have been brought out thus far are the anomalous conduct of meta-nitro-toluene, and the formation of ortho-sulphamine-benzoic acid, instead of benzoic sulphinide, which was expected. It is intended next to take up the study of some xylene derivatives for the purpose of determining, if possible, whether these facts are general in their application.

UNIVERSITY OF TENNESSEE, *April* 6, 1886.

NEW APPARATUS FOR THE ESTIMATION OF CARBONIC ACID IN THE AIR.

BY THOMAS C. VAN NÜYS.

From results of the estimation of carbonic acid in the air since Pettenkoffer[1] published his method, it is evident that either the amount of carbonic acid in the air varies greatly at different times or the methods employed are defective. Later investigations tend to prove that the methods are not reliable, the estimations being too high. Truchot's[2] maximum quantity found in forty-nine estimations made during fine weather was 4.2 volumes in 10,000 volumes of air, and where the ground was covered with snow his maximum quantity was 8.7 volumes. H. and A. Schlaginweit[3] found from 3.2 to 5.8 volumes in 10,000 volumes of air, according to altitude. Mène[4] found 7 volumes in 10,000 volumes of air. On the contrary, G. F. Armstrong[5] claims that the quantity of carbonic acid in the air does not exceed 3.5 volumes in 10,000 volumes of the air, and J. Reiset's[1] maximum quantity in ninety-one estimations was 3.415 volumes in 10,000 volumes of air, the average number of volumes being 2.978. Generally considered, the methods for the estimation of carbonic acid in the air, whether by passing air through tubes containing a solution of barium hydrate, or by shaking up a definite quantity of a standardised solution of barium hydrate with a measured quantity of air, do not provide sufficiently for preventing of contact of the external air containing CO_2 with the $Ba(OH)_2$ when titurated with oxalic acid or when filtered and washed.

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[1] Sitzungsberichte der k. bayerischen Acad. d. Wissenschaft, 1860, 291.

[2] Ann. agronomiques, 1877, 69.

[3] Pogg. Annalen **76**, 442.

[4] Ann. de la société des sciences industrielles de Lyon, Ncs. 1-9, in Rep. Chim. App. IV, 473.

[5] Proceedings Royal Society **30**, 343.

By the apparatus illustrated by the figure it is intended to overcome this difficulty. The capacity of the apparatus *A*, ascertained by having determined its weight when empty and dry, and its weight when filled with distilled water at 4° C., is 6177 cc. The diameter of the mouth *a* of the apparatus is from 22.5 to 25 mm. The inside diameter of the end *b* of the apparatus is 65 mm. This drawn out, part of the apparatus is provided with a glass stop-cock *c*. The stopper *d* fits in the mouth of the apparatus by a ground surface so as to be perfectly air-tight. A hole 4.5 mm. in diameter passes through the stopper closed above by the rubber tube, and below the stopper is drawn out so as to form a tube which is bent and is connected to a piece of glass tubing by means of a rubber tube. The attached piece of tubing is bent upwards and drawn out so its orifice is 4 mm. in transverse diameter and 1.5 mm. perpendicular diameter.

When the stopper is in place, with a small quantity of grease it can be readily turned with the thumb and one finger. The capacity of the flask *B* is 400 cc., and it is provided with a rubber stopper having three holes. Through one of these holes passes the bent glass tube *e*, which is connected with the apparatus; through another hole the tip or dropper of the burette, and through the third hole the bent end of the chlor-calcium tube *f*. This tube is filled with pieces of pumice saturated with a strong solution of natr. hydrate. In estimating the carbonic acid in the air with this apparatus I use a solution of oxalic acid standardised according to Pettenkoffer,[2] and a solution of barium hyd. of one-half the strength of that of Pettenkoffer, thereby avoiding an excess of barium oxalate which makes the disappearance of the red color of the rosolic acid more obscure. 2.8636 grams pure oxalic acid which has neither effloresced nor deliquesced are dissolved in 1000 cc. distilled water. 1 cc. of this solution has the same saturating power as 1 milligram CO_2. About 3.5 grams pure barium hydr. and .5 gram barium chlor. are dissolved in 1000 cc. water. If the solution is not clear it should be filtered. The

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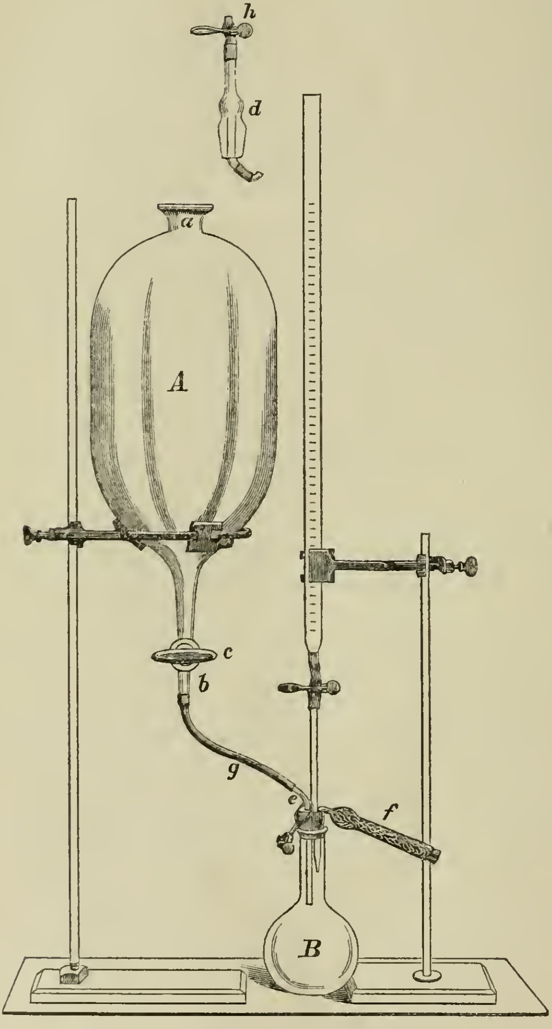
[1] Comptes Rendus **90**, 1144.

[2] Annalen der Chemie, Suppl. Band **2**, 25.



solution should be kept in an aspirator bottle, the stopper of which is connected with a large chlor-calcium tube having its end bent, and the tube filled with pieces of pumice saturated with a strong solution of natr. hydrate. In titurating the Ba hydr. solution with the solution of oxalic acid, contact with the external air is avoided by employing Pettenkoffer's[1] method in filling a pipette. The flask *B* may be employed in this tituration. Two or three drops of an alcohol solution of rosolic acid are introduced into it, the rubber tube *g* is removed from the end of the apparatus and is connected with a wash-bottle containing a solution of natr. hydrate, and a U-shaped tube containing soda-lime. The end of the chlor-calcium tube *f* is connected with an aspirator bottle filled with water, and air is drawn through the apparatus until the flask is filled with air free of CO_2. The end of the rubber tube *g* is taken between the thumb and finger and carefully disconnected and placed over the tip or dropper of a 50 cc. pipette containing the Ba solution, and when the solution has run into the flask, the end of the tube is removed from the pipette with the precaution that no outside air enter the tube. It is fitted over the mouthpiece of a wash-bottle filled with water.[2] About 100 cc. water is passed into the flask through the rubber tube, when it is secured by the pinch-cock. The oxalic acid solution is added until the red color disappears. Titurations should be repeated until an agreement is reached. As the oxalic acid solution is liable to change, titurations should be made every two or three days to avoid the uncertainty of results owing to decomposition of the acid in solution.

The stopper *d* is prepared for use by filling the canal passing through its entire length with water as a pipette is filled when the rubber tube is secured by the pinch-cock. The ground surface of the stopper is then rubbed with grease.

The inside surface of the apparatus *A* is dried, either by washing with absolute alcohol and ether, and let remain open in a warm place until dry, or by attaching the tube *b* to a foot-bellows by means of a rubber tube, and pumping air into it until dry. In this way the apparatus is filled with the air, the CO_2 of which it is intended to estimate.

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[1] Mohr's Titrirmethode, Vierte Auf., 140.

[2] Every case in which water is used which will subsequently come in contact with the Ba solution, distilled water having been boiled is employed.

The flask *B* is dried, and into it are put two or three drops of an alcohol solution of rosolic acid. Air is introduced into it having its carbonic acid separated as before, when the rubber tube *g* is secured by the pinch-cock.

The apparatus having been filled with the air, the carbonic acid of which it is intended to estimate, a thermometer is suspended in the apparatus and let remain thirty minutes, so the temperature may become constant, when the temperature and barometric pressure are noted. 50 cc. of the barium solution are introduced into the apparatus *A*, the glass stop-cock having been closed. The stopper is put in place and secured by means of a rubber band. The apparatus *A* is turned on its side, placed on a table, and by frequent turning the inside surface is kept wet with the solution, and after the lapse of two hours all of the carbonic acid will have been absorbed. The lower end of the apparatus is raised a short distance from the table and the tube *b* is filled with water from the glass stop-cock to the end. The apparatus is returned to its place on the stand, the water remains in the tube, and the end of the rubber tube *g*, which is attached to the glass tube *e*, is filled with water from the part of tube secured by the pinch-cock to the end and fitted over the tube *b*, carefully excluding any air. The pinch-cock is removed to its place, as shown in the figure, and the glass stop-cock is carefully turned. If the air in the apparatus is under less pressure than the outside air, bubbles will pass through the barium solution into the apparatus, in which case the stop-cock should be turned so that the air may pass into the apparatus slowly and all the carbonic acid of the air be absorbed as it comes in contact with the natr. hydrate solution in the chlor-calcium tube. In a short time all of the barium hydrate solution will have passed into the flask. The rubber band or cord which secured the stopper in place is removed. An aspirator bottle containing water is placed one metre above the apparatus, and by means of a rubber tube 6 mm. internal diameter, connection is made between it and the rubber tube *h* attached to the stopper and secured by the pinch-cock. The rubber tubing making this connection should be filled with water to the exclusion of any air. As the pinch-cock is removed from the rubber tube at the stopper the water will flow into the apparatus and is thrown against its surface. By means of the thumb and finger the stopper is turned slowly, so every part of the surface is washed. If the rubber tube should become twisted it can be prevented from turning with the other hand, providing the tube does not fit too tight. By careful washing not more than 250 cc. water will be required, which was determined by introducing 2 cc. strong hydrochloric acid and 40 cc. water, and washing until the acid disappears from the wash-water. The rubber tube *g* is secured by the pinch-cock, and the end is removed from the tube *b*. The bent tube *e* is drawn up so its end comes within 3 cm. of the stopper, and the long tip of the burette is carefully pushed further into the flask, and the barium hydrate is titurated by letting 20.5 cc. of the oxalic acid solution run in from the burette at once, and after gently shaking, one or two drops are added, and so on until the red color disappears. The data of one estimation are here given.

50 cc. of the barium hydr. = 24.5 cc. of the oxalic acid sol. Temperature 4° C. Barometric pressure 743.5 mm.

Capacity of apparatus, ...	6177 cc.
Deduct 50 cc. volumes Ba solution, . .	50
	6127 cc.

This volume, when subjected to normal pressure, would be $= \frac{6127 \cdot 743.5}{760} = 5993.9$ cc., and when reduced from 4° C. to zero would be $= \frac{273 \cdot 5993.9}{277} = 5907.3$ cc. It required 21.1 cc. oxalic acid solution, hence 3.4 milligrams CO_2 (the equivalent of 3.4 cc. oxalic acid solution) found in 5907.3 cc. air at zero and 760 mm. pressure, 1 milligram CO_2 at zero and normal pressure measures 0.5084 cc., hence $3.4 \times 0.5084 = 1.72869$ cc. CO_2 found. To find the number of volumes of CO_2 in 10,000 volumes air we have the following equation:

$$5907.3 : 1.72869 :: 10,000 : x$$

$$x = \frac{1.72869}{5907.3} = 2.926 \text{ volumes in 10,000 volumes air.}$$

Estimations of carbonic acid in the air have been made in this laboratory several weeks under my direction, by Mr. B. F. Adams, who found that the principal source of error is the difficulty of ascertaining the correct temperature. If the apparatus is placed where it is thinly shaded the temperature will vary ten or fifteen degrees C. in 30 minutes, according as the rays of the sun pass through the apparatus or as reflecting bodies are warmed.

Even the temperature varies in different parts of the apparatus. When estimations are made, the temperature being below the freezing-point, and the barium solution is run into the apparatus, which necessarily has a temperature above the freezing-point, the air in the apparatus is warmed unequally. The difficulty is not removed by waiting until the fluid freezes, for during this time some air free of CO_2 may pass out of the apparatus by diffusion, and a false result be reached. With this apparatus, exercising the greatest care in determining the temperature and the atmospheric pressure, we have found that the quantity of CO_2 in the air is subject to slight variation at different times, but at present the number of estimations made is not sufficient to establish the maximum and minimum quantities during night and day, and during different seasons.

INDIANA UNIVERSITY, CHEMICAL LABORATORY, BLOOMINGTON, IND.

ON THE SO-CALLED SILVER SUB-CHLORIDE.

BY SPENCER B. NEWBURY.

A year ago I published a series of experiments[1] on the action of solvents on silver chloride which had been blackened by exposure to light, from which the conclusion was drawn that in the blackening action of light no silver sub-chloride, but only metallic silver is formed. This was shown to be the case by the fact that if blackened silver chloride be treated repeatedly with a concentrated solution of sodium chloride, the silver chloride which has escaped reduction is completely dissolved, and pure, finely divided metallic silver remains.

The existence of silver sub-chloride has generally been assumed by chemists and writers on photography, and the formula Ag_2Cl has been supposed to represent its composition. A very complete outline of the literature of the subject is given by Von Bibra,[2] and need not be repeated here. There may be said to be three methods by which the so-called silver sub-chloride has been prepared, as follows:

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[1] This Journal **6**, No. 6.

[2] Journ. fü prac. Chem., 1875.

1. Cavillier,[1] by passing excess of chlorine into an ammoniacal solution of silver chloride.

2. Wetzlar,[2] by action of iron or copper chloride on metallic silver.

3. Wöhler,[3] by the action of hydrochloric acid on silver sub-oxide or its salts.

In the last case Wöhler prepared silver sub-citrate by heating silver citrate to 100° in a current of hydrogen; he expressly states, however, that the existence of this substance is not proved, since a mixture of metallic silver with undecomposed citrate would behave in a similar manner. By treatment of the sub-chloride with potash and hydrochloric acid respectively, Wöhler obtained the corresponding silver sub-oxide and sub-chloride. No attempts seem to have been made to free these substances from possible admixtures of metallic silver or from unchanged citrate or chloride, in order to render the analysis of them conclusive. Von Bibra[4] prepared the so-called sub-chloride by the three methods given above, and concluded that No. 1 gives true sub-chloride; No. 2, a mixture of silver and silver chloride; No. 3, also true sub-chloride. In the last case Von Bibra assumed the reaction to be complete when the weight of the silver citrate, after heating six to seven hours in a current of hydrogen, remained constant; washed the product with water to remove free citric acid, treated with HCl, assumed the product to be pure silver sub-chloride, and established its formula to be Ag_4Cl_3.

In the hope of preparing the sub-chloride in a pure state by the action of some solvent which should remove possible impurities, I was led to make the following experiments:

1. The method of Cavillier, by action of chlorine on ammoniacal silver solutions, was tested. A stream of dry chlorine was conducted into a solution of silver chloride in ammonia. A slight gray precipitate was gradually formed, which, if the solution was kept strongly ammoniacal, consisted of finely divided silver wholly soluble in nitric acid. If, however, the ammoniacal solution was allowed to become nearly saturated with chlorine, mixtures of silver chloride and metallic silver, in varying proportions, were deposited, which on treatment with NaCl left a residue of gray metallic silver. From this I conclude that no sub-chloride is formed by this reaction. This is not remarkable, since all authorities agree that

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[1] Journ. d. Pharm., 1830. [2] Jahresber., 1828. [3] Ann. Chem. Pharm. **30**. [4] *Loc. cit.*

the hypothetical sub-chloride is decomposed by ammonia, silver chloride being dissolved, and metallic silver remaining. The formation of the sub-chloride in a strongly ammoniacal solution was, therefore, not to be expected. The precipitation of a small quantity of metallic silver is perhaps owing to impurities in the chlorine which exercise a reducing action.

2. Finely divided silver was treated with a cold twenty per cent. solution of cupric chloride. Cuprous chloride was at once formed, but redissolved on addition of large excess of cupric chloride solution, leaving only white silver chloride.

If a few drops of stannous chloride solution are added to a solution of silver nitrate, a precipitate is formed which is at first white, but becomes black on stirring. Analysis of this precipitate showed silver and chlorine in varying proportions. If, however, stannous chloride be added in excess, a white precipitate consisting of silver chloride and a tin compound, probably oxychloride, is formed. If, therefore, dilute silver nitrate solution be gradually added to dilute stannous chloride solution until a dark precipitate begins to form, the precipitate then filtered off, and a further addition of silver nitrate made to the filtrate, a black precipitate is obtained. This was found to be metallic silver. It is evident that it is the stannous nitrate formed in this reaction which reduces the silver after all the chlorine has been precipitated, and also that no silver sub-chloride is formed.

3. I have made a large number of careful experiments on the preparation of silver sub-citrate by heating silver citrate to 100° in a current of hydrogen, following exactly the instructions of Wöhler and Von Bibra. The hydrogen was passed through a red-hot tube, and dried with sulphuric acid and calcium chloride. The silver citrate was very carefully dried in vacuum. Nevertheless, I did not find it impossible to obtain a constant weight as described by Von Bibra, nor to obtain a product of definite composition. Water was always given off, and a gradual decrease in weight took place, more or less rapid according to the rapidity of the stream of hydrogen. The silver citrate was changed to a black powder, under the action of a moderate current of gas, in about two hours, and was then found to have lost about two per cent. of its weight. If the action was continued several hours longer, the mass appeared to be partly fused, had a metallic lustre, and was found in some cases to have lost weight to the

amount of six per cent. On treating the product with water a solution resulted which was red by transmitted light, but invariably gray and cloudy by reflected light. It seems to me highly probable that this red color is caused by finely divided metallic silver. Hydrochloric acid produces in the solution a reddish precipitate, which on analysis was found to consist of silver chloride, with a minute amount of free silver. This shows that even when the action of the hydrogen is continued for several hours there is still a large amount of unchanged citrate present. I have made many attempts to separate the constituents of this black substance by solution in water, but obtained no results, because the red solutions are not clear, and give only silver chloride and traces of silver on treatment with HCl. It is evident that the statement generally contained in the text-books, that the argentous citrate dissolves in water with a red color, is incorrect.

On treating the black powder directly with hydrochloric acid, curdy brown precipitates were obtained, which contained varying proportions of silver and silver chloride, according to the duration of the action of the hydrogen. The substances were analysed by dissolving out the silver chloride by ammonia, and weighing residue of metallic silver. The formula Ag_4Cl_3 requires AgCl 81.8 per cent., Ag 18.2 per cent.; Ag_2Cl requires AgCl 57.1 per cent., Ag 42.9 per cent. Varying proportions of silver were found, according to the length of time treated. In some cases the amount of silver was found to exceed 60 per cent.

The substances obtained by acting upon the reduced citrate with hydrochloric acid were treated with cold solution of sodium chloride. In every case silver chloride was dissolved, and a residue of metallic silver was left. Wöhler, in the article referred to above, states that ammonium chloride solution produces this result. It is therefore evident that if the sub-chloride exists, it is of so unstable a character as to be readily decomposed by the ordinary solvents of silver chloride. There is, in fact, no evidence whatever of the existence of such a compound, or that the substances which have been supposed to be silver sub-chloride are anything but simple mixtures of silver and silver chloride.

In the case of the sub-citrate and sub-oxide the fact that Wöhler and Von Bibra obtained a product of constant weight on heating silver citrate in hydrogen has been assumed to be a proof of the existence of these substances. However, the hypothesis of the formation of silver sub-citrate does not account for the *loss* of weight which has been in every case observed. The replacement of silver by hydrogen, and setting free of citric acid, calls for a gain in weight.

In my own experiments, which have been very numerous, and performed under a variety of conditions, an absolutely constant weight was in no case obtained. Both water and carbon dioxide were given off, in approximately equal quantities, as long as the action of the hydrogen was continued. On exhausting the products with ether a brown, tar-like mass was obtained, which contained free citric acid in considerable quantity, together with other substances which were not identified.

In conclusion, the loss of weight on heating silver citrate in a current of hydrogen, the formation of carbon dioxide, and residue of metallic silver left on treating the products with sodium chloride solution, seem to me to indicate that the reaction in question consists in the separation of silver and decomposition of citric acid, rather than in the formation of silver sub-citrate.

LABORATORY OF CORNELL UNIVERSITY, *March*, 1886.

Contributions from the Chemical Laboratory, U. S. Department of Agriculture.

VII.—KUMYS.

COMMUNICATED BY H. W. WILEY.

Fermented mare's milk has long been a favorite beverage in the East, where it is known as "Kumys." Although the Tartars and other Asiatic tribes use mare's milk for the manufacture of kumys, yet it is not the only kind that can be employed. Since the consumption of milk wine has extended westward, cow's milk is chiefly employed for making it, both in Europe and America. Mare's milk is considered most suitable for fermentation, because of the large percentage of milk sugar which it contains.

Koenig[1] gives as the average percentage of milk sugar in mare's milk 5.31. The same author[2] gives as a mean of 377 analyses of cow's milk 4.81 per cent. of lactose. Dr. Stahlberg,[1] who brought forty mares from the steppes of Russia to Vienna for the purpose of using their milk for kumys, found its percentage of lactose to be 7.26. On the other hand, ordinary mares that were kept at work gave a milk containing only 5.95 per cent. sugar.

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[1] Nahrungsmittel, 46.

[2] *Op. cit.* 40.

The quantity of milk sugar in mare's milk is great, but there is a deficiency of fat and other solids. It appears to contain fully 89 per cent. water, while cow's milk does not have more than 87 per cent.

The process of manufacture is not uniform. In the Orient the mare's milk is placed in leathern vessels; to it is added a portion of the previous brewing, and also a little yeast. In 30 to 48 hours the process is complete. During this time the vessels are frequently shaken.

In the samples analysed by me the milk was treated with a lactic ferment and yeast. After 24 to 48 hours' fermentation the kumys was bottled. The bottles were kept in a cool place, not above 50° F., and in a horizontal position. When shipped to me they were packed in ice. After they were received in the laboratory they were kept on ice until analysed.

Method of Analysis.

Carbon Dioxide.—The estimation of the carbon dioxide was a problem of considerable difficulty. It was evidently impracticable to attempt opening the bottle and determining the gas in a portion of the contents. Fortunately I had access to a large balance which would turn with a milligram. On this I weighed the whole bottle, into the cork of which I had inserted a stop-cock such as used sometimes with a champagne bottle. With the bottle of kumys were also weighed two drying flasks containing concentrated sulphuric acid with their connections. Having obtained the weight of the whole, the gas was allowed to escape slowly from the stop-cock and to bubble through the sulphuric acid in the washing bottles. These, previously to being weighed, were filled with the gas from an ordinary carbonic dioxide generator. After the gas had almost ceased to flow the bottle of kumys was frequently shaken. It was also placed in a pail of water having a temperature of 30° C. After half an hour the gas ceased to come over. The whole apparatus was again weighed. The loss of weight gave the quantity of free carbon dioxide in the sample. After the analysis was completed the volume of the bottle was measured. It is fair to assume that at 30° the kumys still contained an equal volume of dissolved CO_2. In determining the total CO_2 this volume, or its equivalent weight, was added to that obtained by direct determination. By this method the CO_2 dissolved under pressure in the bottles is estimated separately from that which the kumys contains in solution under the weight of one atmosphere. Since it is of no importance to separate the gas into these two portions, I have given it altogether in the tables—in volume—by weight and in percentage by weight.

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[1] Tymowski's Bedeutung des Kumys, 12.

Acidity.—The samples examined showed under the microscope the acetic ferment, and a small portion of the acidity was therefore possibly due to acetic acid. It is the custom in giving the results of analyses of kumys to represent the whole of the acidity as due to lactic acid. The direct titration of the lactic acid in the kumys was attended with such difficulty that the attempt was abandoned. Whatever indicator was employed the change in color was so obscured that no sharp reaction could be obtained. To obviate this trouble the kumys was mixed with an equal volume of saturated solution of magnesium sulphate. After shaking the mixture it was poured through a linen filter. The first portions running through were turbid. After returning these to the filter it was quite clear. Better results were obtained by using with the kumys equal volumes of alcohol. The filtrate from this mixture was uniformly bright. In this filtrate the acid was estimated by titration with a standard sodic hydrate solution, making the proper corrections for dilution and using phenolphthalein as indicator. I would recommend this alcoholic method of clarification to all who may have occasion to determine acid in milk.

Alcohol.—The alcohol was estimated by distilling 500 cc. kumys with 10 cc. water until the distillate amounted to 500 cc. This being still turbid was redistilled with a small quantity of water. The final distillate of 500 cc. was used for the estimation of the alcohol in the usual way—viz.: by taking its specific gravity and calculating the alcohol from tables.

Milk Sugar.—The milk sugar was estimated by the method I recommended in a paper read at the Philadelphia meeting of the American Association for the Advancement of Science.[1]

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[1] This Journal **6**, No. 5.

Fat.—Twenty grams of the kumys were evaporated to dryness in a Schaelchen, the whole rubbed to a fine powder and extracted with ether in a continuous extractor. The process of extraction lasted six hours. These results do not give accurate data for fat, since no allowance was made for the solubility of the lactic acid.

Albuminoids.—The albuminoids were estimated by evaporating five grams of the material in a Schaelchen, rubbing to a fine powder with soda-lime, and burning with the same in the usual way.

Water.—In a flat platinum dish partly filled with washed and dried sand, two grams of material were weighed and dried to a constant weight at 100°. The following are the results of the analyses :

No. of Sample.	Weight of Kumys in Grams.	Volume of CO_2 in Litres.	Weight of CO_2 in Grams.	Per cent. of CO_2 by Weight.	Per cent. of Acidity as Lactic Acid.	Per cent. of Alcohol.	Per cent. of Nitrogen.	Per cent. of Albuminoids.	Per cent. of Fat.	Per cent. of Water.	Per cent. of Milk Sugar.
1	747.415	2.543	5.009	.67	...	.87	.431	2.69	2.21	88.81	4.33
2	729.376	3.140	6.186	.85	.47	.66	.412	2.58	2.15	89.53	4.31
3	768.575	3.179	6.269	.82	.51	.69	.483	3.02	2.07	89.15	4.33
4	736.035	3.281	6.463	.88	.45	.81	.482	3.01	1.99	89.31	4.43
5	746.187	3.579	6.850	.91	.48	.86	.423	2.64	1.67	89.97	4.43
6	750.247	2.973	5.757	.77	.43	.70	.450	2.81	1.75	89.87	4.33
7	738.840	3.204	6.313	.85	.49	.73	.462	2.89	2.44	89.01	4.48
8	752.550	3.263	6.428	.85	...	.77	.450	2.81	2.34	88.87	...
Mean..	......	......	......	.83	.47	.76	.449	2.56	2.08	89.32	4.38

It will be of interest to compare these results with those obtained by other analyses, both with kumys from mare's milk and from other sources. As a mean of fourteen analyses of mare's-milk kumys Koenig[1] gives the following figures—viz.: Water, 92.47 per cent.; alcohol, 1.84 per cent.; lactic acid, .91 per cent.; lactose, 1.24 per cent.; albuminoids, 1.97 per cent.; fat, 1.26 per cent.; ash, .31 per cent.; carbonic acid, .95 per cent.

The mean of two samples of kumys made of cow's milk is given by the same author as follows: Alcohol, 2.64 per cent.; lactic acid, 0.80 per cent.; milk sugar, 3.10 per cent.; albuminoids, 2.02 per cent.; ash, 0.45 per cent.; carbonic acid, 1.03 per cent.

In nine analyses of kumys[2] probably made of cow's milk the means are as follows: Alcohol, 1.38 per cent.; lactic acid, 0.82 per cent.; sugar, 3.95 per cent.; albuminoids, 2.89 per cent.; fat, 0.88 per cent.; ash, 0.53 per cent.; carbonic dioxide, 0.77 per cent.

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[1] Koenig, Nahrungsmittel, 67-68.

[2] *Op. cit.* 68.

Interesting analyses of kumys prepared from mare's milk have also been made by Dr. P. Vieth.[1] The mares from which the milk was taken were on exhibition at the London International Exposition for 1884. These animals were obtained from the steppes of Southeastern Russia. The mares were from five to six years old and were cared for and milked by natives of the country from which they were taken. When milked five times daily the best of these mares gave from four to five litres of milk. It is to be regretted that the milk sugar, the most important ingredient of milk in respect of kumys manufacture, was estimated by difference. Eleven analyses of the mixed milk gave the following numbers:

Table of Analyses.

	Minimum.	Maximum.	Mean.
Sp. Gr.,	1.0335	1.0360	1.0349
Water,	89.74 per cent.	90.41 per cent.	90.06 per cent.
Fat,	0.87	1.25	1.09
Albuminoids,	1.71	2.11	1.89
Milk Sugar,	6.30	6.82	6.65
Ash,	0.26	0.36	0.31

The kumys made from the above milk had the following composition:

Sample No.	1.	2.	3.	4.	5.
Water......	90.99 per ct.	91.95 per ct.	91.79 per ct.	91.87 per ct.	92.38 per ct.
Alcohol	2.47	2.70	2.84	3.29	3.26
Fat	1.08	1.13	1.27	1.17	1.14
Albuminoids	2.25	2.00	1.97	1.99	1.76
Lactic Acid..	0.64	1.16	1.26	0.96	1.03
Milk Sugar...	2.21	0.69	0.51	0.39	0.09
Ash............	0.36	0.37	0.36	0.33	0.34

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[1] Landw. Versuch. Stationen **31**, 353 *et seq.*

Sample No.	6.	7.	8.	9.	Mean.
Water.........	92.42 per ct.	91.42 per ct.	92.04 per ct.	91.99 per ct.	91.87 per ct.
Alcohol	3.29	2.25	2.84	2.81	2.86
Fat	1.20	1.22	1.10	1.44	1.19
Albuminoids	1.87	1.75	1.89	1.69	1.91
Lactic Acid..	1.00	0.70	1.06	1.54	1.04
Milk Sugar...	0.00	2.30	0.73	0.19	0.79
Ash............	0.35	0.36	0.34	0.34	0.35

Collecting the above means together, we have the following

Comparative Table.

No.	Alcohol.	Lactic Acid.	Sugar.	Albuminoids.	Fat.	CO_2.	Water.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
1.	1.84	0.91	1.24	1.97	1.26	0.95	92.47[1]
2.	2.64	0.80	3.10	2.02	0.85	1.03	88.72
3.	1.38	0.82	3.95	2.89	0.88	0.77	89.55[1]
4.	2.86	1.04	0.79	1.91	1.19	......	91.87
5.	0.76	0.47	4.38	2.56	2.08	0.83	89.32

Notes on the Above Table.

1. Mean of 14 analyses of kumys from mare's milk.

2. Mean of 2 analyses of kumys from cow's milk.

3. Mean of 9 analyses of kumys, origin unknown, probably from skimmed cow's milk.

4. Mean of 9 analyses of kumys made from mare's milk, London Exposition of 1884.

5. Mean of 8 analyses of kumys from cow's milk, made by Division of Chemistry, U. S. Department of Agriculture.

The comparison of the above results shows that the American kumys differs from that of other countries in the following points —viz.:

(*a*) The percentage of alcohol is quite low, and as a consequence the percentage of sugar is high.

(*b*) American kumys contains more fat, showing that it has been made from milk from which the cream had not been so carefully removed as in those milks from which the European kumys was made. But this statement is subject to the modification before mentioned in respect of the estimation of fat.

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[1] By difference.

Mare's milk, as will be seen by the above analyses, contains much less fat than that of the cow and more sugar, thus making it more suitable for the production of kumys. Good cow's milk, however, is suitable for the manufacture of kumys after most of the cream has been removed. Should it be desired to make a kumys richer in alcohol, some milk sugar could be added. The samples of kumys analysed were all "young," as will be seen by the notes to follow.

The samples analysed were kindly furnished me by Mr. Julius Haag, of Indianapolis. This kumys makes a delightfully refreshing drink. When drawn from the bottle and poured a few times from glass to glass it becomes thick like whipped cream, and is then most palatable. It is much relished as a beverage, and is highly recommended in cases of imperfect nutrition by physicians. Those desiring to study the therapeutic action of kumys should consult the monographs of Biel,[1] Stahlberg,[2] Landowski[3] and Tymowski.[4]

Notes on Samples of Kumys analysed by Division of Chemistry.

No. 1. Bottled March 24; analysed April 8.
No. 2. Bottled March 25; analysed April 7.
No. 3. Bottled March 25; analysed April 7.
No. 4. Bottled March 24; analysed April 8.
No. 5. Bottled March 27; analysed April 7.
No. 6. Bottled March 28; analysed April 8.
No. 7. Bottled April 1; analysed April 8.
No. 8. Bottled April 1; analysed April 9.

ELECTROLYTIC ESTIMATIONS AND SEPARATIONS.

By Edgar F. Smith and E. B. Knerr.

In Vol. 5 of this Journal, Thomas and Smith described several methods by which they determined bismuth by electrolysis. We have continued this work, and find that from a sulphate solution containing free sulphuric acid the metal can be completely and rapidly deposited by the current.

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[1] Untersuchungen ueber den Kumys und den Stoffwechsel waehrend der Kumyscur.
[2] Kumys, seine physiologische und therapeutische Wirkung. St. Petersburg.
[3] Du Kumys et de son rôle therapeutique.
[4] Zur physiologischen und therapeutischen Bedeutung des Kumys. Muenchen.

Experiment 1.—The volume of liquid was 25 cc., in which were present .0081 gram metallic bismuth and 1 cc. H_2SO_4. Obtained .0081 gram Bi. We employed an electric current, generating 4 cc. oxy-hydrogen gas per minute. The time required for the precipitation was half an hour.

Exp. 2.—Volume of liquid 25 cc. Quantity of bismuth .0081 gram and 1 cc. H_2SO_4. Found .0081 gram Bi. The current produced 4.6 cc. oxy-hydrogen per minute. Half an hour was required for the precipitation.

Exp. 3.—Volume of liquid as in 2. Quantity of bismuth .0041 gram; H_2SO_4 1 cc. The current yielded 1.8 cc. oxy-hydrogen gas per minute. Time, forty-five minutes.

Exp. 4.—Volume of liquid 25 cc. Quantity of bismuth .0229 gram; 1 cc. H_2SO_4. Found .0228 gram Bi. Strength of current 1 cc. oxy-hydrogen gas per minute. Time, two hours.

Exp. 5.—Same as 4, but obtained .0229 gram Bi. Time, one and one-half hours.

These precipitations were made in the cold. The deposited metal was washed with water and alcohol, and then carefully dried in an air-bath.

We were led to try the separation of bismuth from iron under the above conditions. The following results indicate that this is possible in the presence of free sulphuric acid:

No. of Experiment.	Metallic Bi Present.	Metallic Fe Present.	Volume of Solution.	No. of cc. of H_2SO_4.	Bi Found.	Current Strength in cc. of O.-H. Gas per min.	Time Required for Precipitation.
1	.0041 gram.	.0059 gram.	30 cc.	1	.0040 gram.	.8	1 hour.
2	"	"	30	1	.0041	1.2	35 min.
3	"	"	30	1	.0041	1.2	1 hour.
4	.0082 gram.	"	35	1	.0082	.8	1¼ hrs.
5	"	"	40	2	.0082	1.4	2 hrs.
6	"	"	40	2	.0082	1.4	3½ hrs.
7	"	"	40	2	.0082	1.4	2 hrs.
8	.0041 gram.	"	30	2	.0040	1.2	2 hrs.

The iron was present as ferrous sulphate. In the following tests it existed as ferric-ammonium sulphate.

9	.0041 gram.	.0230 gram.	30 cc.	2 cc.	.0041 gram.	2.5	1 hour.
10	“	“	30	2	.0041	2.5	1 hour.
11	“	“	40	2	.0041	1.2	1 hour.
12	.1145 gram.	.0230 gram.	150	3	.1129	3	3 hrs.
13	.1542	“	150	3	.1538	3	3 hrs.
14	.1285	“	150	3	.1285	3	3 hrs.
15	.1285	“	150	3	.1281	3	3 hrs.

Bismuth can also be separated from nickel and cobalt under similar conditions. Our record of results shows the following:

No. of Experiment.	Metallic Bi Present.	Metallic Cobalt Present.	Metallic Nickel Present.	Volume of Solution.	No. of Free cc. H_2SO_4.	Metallic Bi Found.	Current Strength in cc. of O.-H. gas per Minute.	Time Allowed for Precipitation.
	Gram.	Gram.	Gram.			Gram.		
1	.0041	.0104	……	20 cc.	2	.0041	3.5	40 minutes.
2	“	“	……	20	2	.0041	3.5	30 “
3	“	“	……	25	3	.0041	3.5	2 hours.
4	.0229	……	.0219	25	3	.0229	1	2 “
5	.0229	.0104	……	25	2	.0231	1.4	2 “
6	“	……	.0219	30	2	.0229	1	2 “

In all these experiments the filtrates from the deposited metal were examined for bismuth, and the precipitated metal for the others which were present in the solution with it. Although in Experiment 5 the amount of the bismuth is slightly in excess, no cobalt was discovered with it.

Manganese can also be included in the list of metals from which bismuth may be separated by electrolysis.

No. of Experiment.	Metallic Bi Present.	Metallic Mn Present.	Volume of Solution.	No. of cc. of Free H_2SO_4.	Grams Bi Found.	Strength of Current in cc. O.-H. Gas per Minute.	Time Required for Precipitation.
1	.0229 gram.	.0236 gram.	50 cc.	2	.0229 gram.	3	2 hours.
2	.0229	.0236	20	2	.0229	1	2 “
3	.0229	.0236	20	2	.0229	1	1½ “

The deep purple color of permanganic acid appeared at the positive pole and was imparted to the entire solution.

Experiments were tried with solutions containing bismuth and zinc, bismuth and cadmium, bismuth and uranium, and several in which three or four metals, finally, also, one in which nine metals, were present with a definite amount of bismuth.

No. of Experiment.	Metallic Bi Present.	Al_2O_3 Present.	Cr_2O_3 Present.	Metallic Fe.	Metallic Co.	Metallic Ni.	Metallic Cd.	Metallic Mn.
	Gram.	Gram.	Gram.	Gram.	Gram.	Gram.	Gram.	Gram.
1	.0229	......	......	......	......	......	......	......
2	"	......	......	......	......	.....	......	......
3	"	......	......	......	......	......	......	......
4	"	......	......	......	......	......	.0057	......
5	"	......	......	......	......	......	......	......
6	"	......	......	......	......	......	......	......
7	"	......	......	......	......	......	......	......
8	"	.0124	.0063	......	.0104	.0219	......	......
9	"	.0124	.0126	.0230	.0140	.0219	......	......
10	.0229	.0124	.0126	.0230	.0140	.0219	.0057	.0236

No. of Experiment.	Metallic Ur.	Metallic Zn.	Volume of Solution.	Free cc. H_2SO_4.	Bi Found.	Strength of Current in cc. O.-H. Gas per Minute.	Time.
	Gram.	Gram.			Gram.		
1	......	.0393	20 cc.	2	.0223	1	2 hours.
2	......	"	20	2	.0224	1	3 "
3	......	......	50	2	.0227	1.1	1¾ "
4	......	......	50	2	.0229	1.1	1⅓ "
5	.0099	......	20	1	.0229	2	¾ "
6	"	......	20	1	.0225	2	35 minutes.
7	"	......	20	1	.0229	2	50 "
8	......	.0393	100	3	.0229	1.4	2 hours.
9	......	.0393	100	5	.0229	3	2 "
10	.0099	.0393	150	3	.0229	1.2	4 "

In the *Berichte der deutschen chemischen Gesellschaft* **19**, 325, attention has been called to the fact that mercury in a nitric acid solution can be determined with great accuracy in the electrolytic way. More than a year ago Mr. W. S. Hoskinson, of this laboratory, obtained the following results, using a mercurous nitrate solution:

	Hg required.	Hg obtained.
1	.0141 gram.	.0139 gram.
2	...	.0138
3	...	.0139
4	...	.0139
5	...	.0139

As the strength of the electric current employed in these determinations was not considered, we took occasion to ascertain this fact by additional experiments with similar solutions. Our record shows the following data:

No. of Experiment.	Hg Present.	Hg Found.	Volume of Solution.	Cc. of Free HNO_3.	Strength of Current in cc. of O.-H. Gas per Minute.	Time.
1	.0911 gram.	.0908 gram.	25 cc.	1	4.3	30 minutes.
2	"	.0911	25	½	4	30 "
3	"	"	25	"	4	45 "
4	"	"	25	"	4	45 "
5	"	"	30	"	4	45 "
6	"	.0912	30	"	4	45 "

The mercury separated as a compact, shining deposit; it was washed with water and alcohol, and dried over sulphuric acid.

Yver[1] recommends an acetate solution containing free acetic acid when separating zinc and cadmium by the electric current. Eliasberg[2] has since directed attention to the necessary current-strength in order that the method may be rendered more successful. We have employed this method in about thirty separations of these two metals, and would emphasise the fact that the current should be carefully regulated. Some experience is requisite to insure satisfactory results. Our best results were obtained from a current generating not much more than .1 cc. oxy-hydrogen gas per minute. This is less than that given by Eliasberg. Our separations were made in crucibles of about 40 cc. capacity.

With the tartrates of zinc and cadmium we hoped to get better results. We first operated with a solution containing a definite quantity of cadmium, together with a slight excess of tartaric acid. The electric current employed produced 3.4 cc. oxy-hydrogen gas per minute. Heat was applied to the solution. .0060 gram metallic cadmium was deposited in about forty-five minutes. We subsequently electrolysed a solution of 40 cc. volume, containing .0060 gram Cd and .0185 gram Zn, together with 2 grams of sodium tartrate, and an excess of tartaric acid. After the current, generating .5 cc. oxy-hydrogen gas per minute, had acted for three hours, we obtained .0060 gram cadmium. The metal was not only fully precipitated, but was free of zinc.

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[1] Bulletin **34**, 18.

[2] Zeitschrift für anal. Chemie **24**, 548.

Additional experiments:

1. With the same quantities of cadmium and zinc as above we got .0057 gram Cd. Current = .4 cc. oxy-hydrogen gas per minute.

2. Same as 1. Current = .4 cc. oxy-hydrogen gas. Time, 2½ hours. Found .0054 gram Cd.

3. Same as 2. Time, 4 hours. Obtained .0060 gram Cd.

4. Same as 3. Current = .5 cc. oxy-hydrogen gas. Found .0060 gram Cd.

5. Volume of solution 60 cc., in which there were .0120 gram Cd and .0185 gram Zn, 2 grams sod. tartrate, and an excess of tartaric acid. Current = .5 cc. oxy-hydrogen gas per minute. Time, 4½ hours. Found .0115 gram Cd, free from zinc.

6. With same conditions as in 5, obtained .0116 gram Cd.

The deposition of metal was very rapid at first. The last traces are, however, difficult to remove.

WITTENBERG COLLEGE, SPRINGFIELD, O., *May* 6, 1886.

ON THE DETERMINATION OF ABSOLUTE NEUTRALITY.

BY J. R. DUGGAN.

As some confusion exists in the use of the terms "acidity" and "alkalinity," it seems necessary to state the exact sense in which they are used in this article. It is customary to consider alkalinity as having some connection with the property of certain bodies to combine with acids to form salts and water, but this is more properly called basicity, and it is by no means necessary that a base should be alkaline, or that an alkaline body should be a base. Sodium carbonate is distinctly alkaline, but does not combine with acids, while phenol, which even has acid properties, will, under proper conditions, unite with an acid to form a salt and water. With the term acidity the difficulty is greater, because there is no other word in common use that may be used to express one of its meanings. There certainly are bodies, however, that show acid properties, but do not unite with bases to form salts, as many salts of the heavy metals; while other bodies that are neutral or slightly alkaline will unite with bases to form salts and water, as, for example, primary alcohols. In fact, a certain substance may act as an acid or base according to circumstances, but it cannot show both acidity and alkalinity. Unless otherwise stated, the term acidity when used in this article means the opposite of alkalinity, rather than of basicity. The necessity for this distinction will, I hope, be better appreciated when the following experiments are taken into account. It must not be understood from the above that the acidity of *acids* and the alkalinity of *bases* has no connection with the *avidity to combine* or *affinity* which acids show for bases and bases for acids.[1]

The Influence of Mono- and Polybasic Acids, in the Presence of their Sodium Salts, on the Conversion of Starch by Diastase.

These experiments were undertaken in order to compare the action of organic acids and alcohols on soluble ferments with their action on organised ferments, and are a continuation of some former studies on the relation between chemical constitution and physiological action.[2] One of the principal objects in the work was to ascertain whether or not the action of acids on diastase was proportional to their affinity. Diastase was selected because it is a typical soluble ferment, and one whose action in converting starch into dextrin and sugar is comparatively simple and easily measured. As some of the results obtained are of chemical interest, aside from any connection they may have with physiology, it seems best to consider these separately. As the subject is still under investigation, what is contained in this article must be taken to a certain extent as a preliminary notice.

The amount of acid necessary to retard the action of diastase has been investigated by several observers, and with widely different results in each case; but the recent work of Chittenden and Cummins[3] has shown that this is due for the most part to the fact that different specimens of malt-extract and starch contain varying amounts of proteid matter, which combines with the acid and prevents its retarding action. They find that the acid proteids which are thus formed may even accelerate the action of the ferment. I have found that the normal salts of many acids also prevent the retarding influence of acids, just as they retard or prevent the action of acids in inverting cane-sugar.[1] By preparing reagents as free as possible from foreign substances, and using very dilute starch-paste, I have been able to reduce the amount of even comparatively weak acids, such as formic, that is necessary to distinctly retard diastatic action, to 0.0002 per cent. (1 to 500,000), while 0.001 per cent. entirely prevented action. It is evident from this that the common statement that diastase acts best in a slightly acid solution applies only to such as contains proteids or salts with which the acid may combine, and not remain free to act on the diastase. If it were possible to prepare both starch and diastase perfectly pure, it is probable that any appreciable quantity of the stronger acids would prevent the action of the ferment.

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[1] See Muir's Principles of Chemistry, p. 401 *et seq.*

[2] This Journal **7**, 62.

[3] Studies Lab. Physiol. Chem. Yale College, 1884–5, p. 36.

The influence of alkalis on diastase is even more marked than that of acids; so it will be seen that it is an extremely delicate indicator of acid or alkaline reaction. The practice of using litmus, phenolphthalein, and similar substances, for this purpose is so common that we fall into the belief that they show absolute neutrality; but this is by no means true, and a disregard of this point must lead to grave errors in chemical and physiological investigations. A number of substances will react acid with one indicator and alkaline with another, as, for example, di-sodium phosphate;[2] or we may have an acid or base that is too weak to affect the indicator, as boric acid or urea, in which case the solution will appear neutral when it is not. We may also have a strong acid combined with such a base, or *vice versa*, so that the acid will act on the indicator as though it were uncombined, but it certainly does not act in many chemical reactions or on living organisms in such a manner. As an example, sodium borate or carbonate acts on some indicators as caustic soda, and can be titrated as such, but a more striking illustration is the titration by means of phenolphthalein of the acid combined with alkaloids as free acid.[3] While sodium borate and carbonate are alkaline, they are certainly not as much so as caustic soda, and the same is true of the acid in morphine sulphate and similar salts of the alkaloids. With nearly all indicators the presence of proteid matter does not affect the accuracy with which acids may be determined, but, as already mentioned, the work of Chittenden and Cummins has shown that there is present in such cases a compound which acts entirely differently from the free acid. By the selection of indicators to suit the conditions something may be done to avoid these difficulties, but there will still remain many cases of acidity or alkalinity which cannot be measured by any of the ordinary methods. Ostwald[1] has shown that each acid has a definite strength or affinity-constant which conditions the specific intensity of any action brought about by that acid. This constant may be determined by several methods, the most reliable, since it is free from secondary reactions, being based on the rate at which the acid inverts cane-sugar. It appears that each base also has its affinity-constant, although the methods by which this may be determined are not so well developed as in the case of acids. Let us now suppose that two salts are formed by the addition of two acids to a base, as sodium chloride and sodium acetate. These salts are neutral to all color indicators; and if this neutrality is absolute, it would seem that an equivalent of any acid can neutralise, and is neutralised by, an equivalent of any base without regard to its affinity, for these two acids differ greatly in this respect. This is the same as saying that the acid properties of an acid, and the alkaline properties of a base, are entirely destroyed when the two combine to form a normal salt. That such is not the case may be shown with the ordinary color indicators, but only when there is very great difference in the affinities of the base and acid, as with alkaline carbonates or sulphates of some of the heavy metals. That sodium chloride does not turn blue litmus red, and sodium acetate the reverse, is due to the fact that litmus is not sufficiently delicate as an indicator to respond to the comparatively weak acid and alkaline reactions of these salts. That the salts are respectively acid and alkaline is shown beyond doubt by the investigations of Löwenthal and Lenssen,[2] and more especially of Spohr,[3] on the inversion of cane-sugar, and by their influence on diastatic action in the presence of acids. The addition of sodium chloride to hydrochloric acid increases the rate at which it inverts cane-sugar, while sodium acetate has an opposite effect on acetic acid. The amount of hydrochloric acid required to retard to a certain extent (50 per cent.) the action of diastase is so small that it is difficult to say if this is diminished by the addition of sodium chloride; but the increase in the amount of acetic acid that is made necessary by the addition of sodium acetate is very marked, and is proportional to the amount of the salt added. This is very well shown by the following table. The amount of conversion with diastase and starch-paste alone is shown by the control experiment. The solutions were in each case made up to 100 cc., and the flasks containing them were kept in a water-bath at 55° C. for thirty minutes, when the action of the ferment was stopped by the addition of an excess of caustic soda. The amount of sugar formed was determined volumetrically by Fehling's solution, and calculated as maltose.[1]

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[1] Jour. f. prak. Chem. **85**, 321, and (2) **32**, 32.

[2] Compt. Rend. de l'Acad. **100**, 55.

[3] Jour. Pharm. (5) **11**, 425.

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[1] Jour. f. prak. Chem. (2) **29**, 57.

[2] *Ibid.* **85**, 321, 401.

[3] *Ibid.* (2) **32**, 32.

TABLE I.

	NaOH.	$C_2H_4O_2$.	Maltose.	Per cent. of retardation.
1	.000 gram.	.000 gram.	.420 gram.	...
2	.000	.001	.204	51.4
3	.005	.045	.215	48.8
4	.010	.090	.213	49.3
5	.015	.135	.210	50.0
6	.020	.180	.210	50.0
7	.030	.270	.207	50.7
8	.040	.360	.205	51.2

It will be seen that the retardation is not quite constant, but increases slightly with the amount of alkali and acid present. This is probably due to the action of the substances aside from any condition of alkalinity or acidity. This secondary action, as it may for convenience be called, is very marked with some substances, such as salts of the heavy metals, and when such is the case, of course the reaction cannot be used to measure alkalinity or acidity; but with the alkali metals and most organic substances, the error from this source is very small unless they are used in large quantities. If the retarding action of any substance is partially or entirely prevented by the presence of an acid, it seems fair to conclude that it is to that extent due to alkalinity of the substance, and *vice versa;* but when it is not affected by either acids or alkalis, it is evident that it acts on the ferment in some other manner.

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[1] For greater details of the method used in determining diastatic action, see this Journal **7**, 306.

The table shows that in the presence of 5 mgrs. of caustic soda, 45 mgrs. of acetic acid are necessary to produce the amount of retardation caused by 1 mgr. acting on the starch and diastase alone. (Of course the use of reagents of greater or less purity will cause the amount of acid to vary, so that more or less than 1 mgr. may be required; and with perfectly pure materials, it is impossible to say to what extent this would be reduced.) Now 7.5 mgrs., or one-sixth of the 45 mgrs. of acid, combine with the 5 mgrs. of caustic soda to form normal sodium acetate; and we must suppose that this normal salt neutralises to a certain extent the remaining 37.5 mgrs., or five equivalents of acid. In order to do this sodium acetate must be an alkaline salt, or one in which the affinity of the acid is less than that of the base. The following table shows this to be the case:

TABLE II.

	NaOH.	$C_2H_4O_2$.		Maltose.	Per cent. of retardation.
1	...	...		0.428 gram.	...
2	0.020 gram.	0.015 gram =	½ equiv.	0.000	100
3	"	0.030	1 "	0.363	15.0
4	"	0.060	2 "	0.428	.00
5	"	0.090	3 "	0.396	7.5
6	"	0.120	4 "	0.360	15.9
7	"	0.150	5 "	0.290	32.2
8	"	0.180	6 "	0.225	47.4
9	"	0.210	7 "	0.152	64.5

The second experiment of this series is introduced to show that an excess of caustic soda acts as though there were no acetate present; that is, that the normal salt does not prevent the action of alkalis as it does that of acids. In this case one-half the soda combines with the acid, leaving 10 mgrs. free; but if such an amount of acid is used that only 1 mgr. is left free, the result would be the same, no action taking place. In the third experiment the acid and base were added in the proportion of their combined weights, so there was present only the normal salt. This retards the reaction 15 per cent.; but when another equivalent of acid is added, as in No. 4, the conversion is the same as in the control experiment, showing that the solution is neutral. When more than two equivalents of acid are added, we again get retardation from acidity.

If, now, formic acid is used instead of acetic, a similar series is obtained, except that the retardation from the normal salt is not so great, and the excess of acid required to prevent retardation is considerably less. With propionic acid the reverse is the case, the retardation from the normal salt being greater, and more than two equivalents of acid to one of base being necessary to prevent retardation. It is evident from this that in sodium formate the alkali is more nearly neutralised than in the acetate, while it is less so in the propionate. It will be seen from this that this reaction can be utilised to determine the power that different acids have for neutralising an alkali. Instead of determining the excess of acid which was necessary to neutralise the normal salt, it was found that more accurate results could be obtained, without affecting the proportion, by finding the amount required to retard the reaction 50 per cent. As a standard for comparison a flask containing five equivalents of acetic to one of sodium acetate was used, instead of one containing only diastase and starch. This retarded about 50 per cent., but as it was desirable simply to compare the acids among themselves, the actual degree of retardation was of little importance. The amounts of various acids in excess of the one equivalent which combined with the caustic soda to form the normal salt, which were necessary to produce the same retardation as the five equivalents of acetic, are given in the first column of Table III. They are for convenience expressed in their caustic soda equivalents in the second column. The figures are the amounts required with 20 mgrs. of caustic soda, as this was the amount generally used, but in some of the series 40 mgrs. were used. The results are the mean of several series.

TABLE III.

Acid.	Required Amount.	NaOH Equivalent.
Formic,	14.4 milligrams.	12.5 milligrams.
Acetic,	150	100
Propionic,	246	133
Isobutyric,	273	124
Lactic,	27.0	12.0
Benzoic,	82.4	27.0
Phenylacetic,	129	38.0
Oxalic,	6.30	5.60
Succinic,	109	74.0
Pyrotartaric,	99.0	60.0

Malic,	38.5	23.0
Tartaric,	18.4	9.80
Fumaric,	18.3	12.6
Phthalic 1 : 2,	42.5	20.5
Citric,	46.4	29.0

These figures represent the amount of each acid necessary to produce a certain degree of acidity in a solution which contains the amount of salt formed by the combination of the acid with 20 mgrs. of caustic soda. Of course the affinity of each of the acids is less than that of caustic soda. If acids having a coefficient of affinity greater than that of the base were used, it would then become necessary to use a certain amount of some alkali to prevent the retardation caused by the normal salt, since it would be acid. This part of the subject has not yet been investigated, except to a very slight extent.

The neutralisation of an alkaline base by an acid of lower affinity may be divided into two stages—the saturation of the base to form a normal salt, and the neutralisation of the alkaline salt. The amount of acid necessary to accomplish the first of these depends, of course, upon its combining weight and the number of replaceable hydrogen atoms it contains. In order to determine if the amount required in the second stage depends upon the affinity of the acid, the following experiments were made. Since, according to Ostwald,[1] the power which an acid shows in inverting cane-sugar is the most reliable measure of its affinity, I determined the amount of each of the acids that is required to convert a given amount of cane-sugar under fixed conditions. 10 cc. of a 20 per cent. solution of cane-sugar was, in each case, made up to 50 cc. by the addition of the acid and water. The solutions were heated to 70° C. before mixing, and kept in a water-bath at this temperature for thirty minutes. The reaction was stopped by the addition of a slight excess of caustic soda, and the sugar determined by Fehling's solution as dextrose. The standard for comparison was in each series a flask containing the above amount of sugar and 0.150 gram of acetic acid. By using this as a control experiment, any slight variation in time or temperature caused no error, as all the flasks were under the same conditions. The first column in Table IV shows the amount of each acid required to produce the same amount of conversion as 0.150 gram of acetic. In the second column the acids are expressed in their soda equivalents, while the third is a repetition, for comparison, of the second column of Table III. The fourth column gives the percentage proportion between the figures in the second and third columns, those in the second being taken as 100.

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[1] *Loc. cit.*

TABLE IV.

	Inversion of Cane Sugar.			
Acid.	Required amount.	NaOH equivalent.	NaOH equiv. of am't req'd to neutralise the normal salt.	Per cent. proportion.
Monobasic.				
Formic,	13.8 mgrs.	12.0 mgrs.	12.5 mgrs.	104
Acetic,	150	100	100	100
Propionic,	255	138	133	96.4
Isobutyric,	286	130	124	95.4
Lactic,	26.1	11.6	12.0	103
Benzoic,	85.0	27.9	27.0	96.4
Phenylacetic,	125	37.3	38.0	102
Dibasic.				
Oxalic,	3.71	3.30	5.60	169
Succinic,	66.4	45.0	74.0	164
Pyrotartaric,	57.8	35.0	60.0	171
Malic,	20.8	12.4	23.0	(185)
Tartaric,	10.9	5.80	9.80	169
Fumaric,	10.9	7.50	12.6	168
Phthalic 1 : 2,	11.6	5.60	20 5	366
Tribasic.				
Citric,	15.7	9.80	29.0	296

It is evident from this table that the amount of a monobasic acid required to neutralise an alkaline salt of that acid is proportional to its affinity as measured by its action on cane-sugar. Spohr has reached practically the same conclusion from his study of the influence of normal salts on the inversion of cane-sugar by acids.[1] In the case of dibasic acids the table shows that more is required to neutralise the salt than with monobasic acids, or that the normal salt is more alkaline than it would be if formed from a monobasic acid of the same affinity-constant. For example, it was found that normal sodium succinate retards the action of diastase more than an equivalent quantity of sodium acetate, although succinic acid inverts sugar more rapidly than acetic, and might therefore be supposed to form a less alkaline salt. It must be remembered that in comparing the action of acids, the carboxyl groups are compared, so that half an equivalent is used in the case of dibasic acids. To explain this greater alkalinity of salts of dibasic acids, we must suppose that each atom of sodium not only neutralises the carboxyl group into which it enters, but influences in some manner the other similar group in the molecule. There is reason to suppose that a molecule of oxalic acid inverts cane-sugar more rapidly than would two molecules of an acid having the formula COOH, or that the affinity of polybasic acids is increased by a mutual reaction between the carboxyl groups.[1] This being true, it follows that the neutralisation of one carboxyl group in such an acid must diminish the affinity of the remaining ones. In the case of phthalic acid this action is much more marked than with acids of the paraffin series. This cannot be due to experimental error, as this acid was examined very carefully; but it will be necessary to examine other acids in which we have what is termed the ring structure before attempting any explanation of this. In the case of the one tribasic acid examined, the amount of acid required to neutralise the salt is, as would be supposed, more than with either mono- or dibasic. As all of these results were obtained from the use of a monacid base, it does not follow that they would hold good for a polyacid base.

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[1] Jour. f. prak. Chem. (2) **32**, 46.

This greater alkalinity of salts of polybasic acids is very well shown in the case of phosphoric acid, for although a molecule of this acid converts sugar more rapidly than three molecules of acetic, it is with considerable difficulty that the acid can be made to form a normal sodium salt. In other words, the acidity of the acid is so well neutralised by one or two atoms of sodium that it is only with difficulty that it can hold a third. The reverse of this tendency of the weaker polybasic acids to form only primary or secondary salts is seen in the frequent formation of basic salts when a strong acid combines with a slightly alkaline base.

The Influence of Alcohols on Diastatic Action.

In the presence of about 7 per cent. by weight of ethyl alcohol the action of diastase is retarded one-half, but if there is added to 100 cc. of the solution about 3 mgrs. of acetic acid, there is but little retardation. That the retardation by the alcohol which is prevented by this minute quantity of acid is due to its alkalinity is borne out by the fact that the inversion of cane-sugar by acids is also retarded by the presence of alcohol. Titration before and after the experiment showed that there was no etherification, as would be supposed, considering the extreme dilution of the acid. It seems natural to conclude from this that there is here a condition similar to a basic salt in which a great many molecules of the base are combined with one of acid, for if such is not the case, it is difficult to explain the action of the acid in neutralising the alcohol. Under these conditions the alcohol shows alkaline, but not basic properties, since it does not unite with the acid to form an ester (salt). This action of alcohols is of considerable physiological interest, and I hope by further study to throw some light on their action on the living organism. As we approach the acid-phenols through the secondary and tertiary alcohols we find that they act less and less on diastase, until phenol is reached, when we get decided action from its acidity. I hope to verify the results I have obtained by a further study of the influence of alcohols on the inversion of cane-sugar by acids, and until that is done, a lengthy discussion, including the different alcohols, would be premature.

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[1] Muir's Principles of Chemistry, 470.

As the value of any method depends to a great extent upon its accuracy, it will be well to notice the experimental errors that show themselves in the above determinations. An examination of the fourth column of Table IV shows that these may amount to several per cent. Of course, any impurity in the acid is likely to produce an error, and this is probably the cause of the rather large amount of malic acid required to neutralise the normal salt. In the experiments with diastase there is probably a small amount of the acid used up in combining with the proteid matter and salts which cannot be entirely removed from the starch and diastase solution. It will be seen that rather more of the acids which have a high affinity constant is required than the theory calls for. As they are used in small amounts, any proteid matter present would render inactive a proportionately larger quantity of these than of the weaker acids. Ostwald has shown that the results obtained from the inversion of cane-sugar depend to a slight extent on the concentration of the solutions used. When the errors from these and other causes happen to be all on the same side, it is not surprising that they should amount to several per cent. I think the results obtained, however, show that the method is valuable, and will assist in the important work that Ostwald has undertaken. It cannot be doubted that the physiological action of organic acids is dependent to a great extent on their affinity, and the determination of affinity-constants will probably be of as much value to physiological as to pure chemistry.

In conclusion, I do not think it will be out of place to offer a protest against the custom of calling salts acid or neutral according to whether a part or all of the hydrogen is replaced. Primary or mono-sodium carbonate is not an acid salt, nor is the normal salt neutral. This is an extreme case, but it is taken to show that such a use of these terms is incorrect even if we use only the ordinary color indicators.

I am under many obligations to Prof. Remsen for suggestions and for advice which he has kindly given me during the progress of the work.

JOHNS HOPKINS UNIVERSITY, BALTIMORE, *May*, 1886.

NOTE.

Etched Figures and Arrangement of Atoms.

The method of "etched figures," which within the past few years has proved so successful in the detection of hemihedral and tetartohedral forms on crystals which appear to be holohedral, bids fair to play some part in the discussion regarding the position of the atoms in the molecules of crystalline substances.

When Linnaeite (Co_3S_4) is treated with acids its cubic faces are most readily attacked. When treated with fused potash, however, the solution takes place most rapidly in the direction of the dodecahedral planes.

This fact leads F. Becke[1] to observe that probably the cobalt atoms in the molecule are turned towards the cubic faces and the sulphur atoms towards the dodecahedral faces.

Whether the use of this method will throw any light on the position of the atoms in space, is doubtful. It is probable, however, that it will help to an understanding of the forces which act in the formation of crystals.

W. S. B.

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[1] Tschermak's Min. und Petrogr. Mitt. 8, 195.

Vol. VIII. [August, 1886.] No. 4.

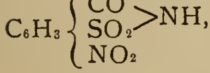
AMERICAN CHEMICAL JOURNAL.

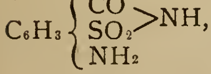
INVESTIGATIONS ON THE SULPHINIDES.

II.—ON BENZOIC SULPHINIDE.[1]

By Ira Remsen and A. G. Palmer.

In the first paper[2] of this series it was shown that the salts derived from phthalic sulphinide are formed by the substitution of the imide hydrogen by metallic elements, and it was suggested that in all probability it would be found that the salts of other sulphinides are formed in the same way. This view has been fully confirmed by subsequent investigations in this laboratory; and the results reached by Noyes[3] in investigating nitro-benzoic-sulphinide,


$C_6H_3\left\{\begin{array}{l}\left.\begin{array}{l}CO\\SO_2\end{array}\right>NH,\\NO_2\end{array}\right.$ and amido-benzoic-sulphinide,


$C_6H_3\left\{\begin{array}{l}\left.\begin{array}{l}CO\\SO_2\end{array}\right>NH,\\NH_2\end{array}\right.$ lend additional support to the view.

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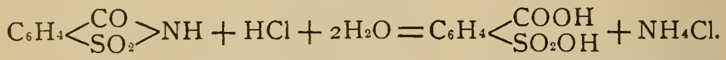
[1] This substance has recently come into some prominence under the name "saccharin," which is given to it on account of its sweet taste. In the notices of saccharin, even in scientific journals, the statement is constantly made that the substance was discovered by Fahlberg. The statement needs modification. As a matter of fact, the substance came to light in the course of an investigation which Fahlberg undertook at my suggestion, and carried on under my direction, and it was first described in a paper by myself and Fahlberg which appeared in the Berichte der deutschen chemischen Gesellschaft, Band 12, S. 469. A more detailed account of the investigation was published later in this Journal, Vol. I, p. 426.—I. R.

[2] This Journal **6**, 260.

[3] *Ibid.* **8**, 167.

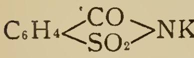
The sulphinide used in the experiments described below was prepared by oxidation of ortho-toluene-sulphamide with potassium permanganate in the usual way. The ortho-toluene-sulphonic acid was prepared by eliminating the nitro-group from nitro-toluene-sulphonic acid by making the diazo-compound and boiling it with alcohol.[1] In regard to benzoic sulphinide a few facts hitherto unknown have been observed. It was found that it can be sublimed without undergoing decomposition, forming thin, elongated, triangular plates. When an aqueous solution of benzoic sulphinide is rendered strongly acid with concentrated hydrochloric acid, and then evaporated almost to dryness on a water-bath, the substance is transformed into ortho-sulpho-benzoic acid, thus:



$$C_6H_4<\begin{smallmatrix}CO\\SO_2\end{smallmatrix}>NH + HCl + 2H_2O = C_6H_4<\begin{smallmatrix}COOH\\SO_2OH\end{smallmatrix} + NH_4Cl.$$

In order to prove that the product was really the sulphonic acid, it was converted into the sodium salt, which was then treated successively with phosphorus pentachloride and ammonia. Almost the theoretical quantity of the sulphinide was thus obtained. When a solution of the sulphinide is boiled with a concentrated solution of barium hydroxide, ammonia is given off, and the barium salt of ortho-sulpho-benzoic acid is formed. From the solution the free acid is easily obtained by precipitating the barium exactly by means of sulphuric acid, and evaporating on the water-bath. From the concentrated solution the free acid separates in white, spear-shaped crystals.

Potassium anhydro-sulphamine-benzoate,



$C_6H_4<\begin{smallmatrix}CO\\SO_2\end{smallmatrix}>NK + H_2O$.—A weighed quantity of benzoic sulphinide was dissolved in water, and to it was added a weighed quantity of pure anhydrous potassium carbonate containing the quantity of potassium requisite to form a salt of the above formula. The salt is extremely soluble in water, and it was necessary to evaporate the solution to almost a syrupy consistency before crystals could be obtained from it. On cooling, short, hard, lustrous, prismatic crystals were deposited. These were filtered off and washed with strong alcohol, dried in the air and analysed.

0.2318 gram air-dried salt lost 0.015 gram H_2O at 120°. When heated to 200° it lost no more.

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[1] See page 243.

	Calculated.	Found.
$C_6H_4<\substack{CO\\SO_2}>NK$	...	...
H_2O	7.52	6.90

I. 0.2168 gram anhydrous salt gave 0.0854 gram K_2SO_4.
II. 0.2594 gram anhydrous salt gave 0.1022 gram K_2SO_4.

	Calculated.		Found.	
$C_7H_4SO_3N$	182	82.35	...	...
K	39	17.65	17.68	17.68
	221	100.00		

Silver anhydro-sulphamine-benzoate, $C_6H_4<\substack{CO\\SO_2}>NAg$.—This salt was obtained as a crystalline precipitate by adding a solution of silver nitrate to a warm solution of the sulphinide. It separates almost completely on cooling. It was filtered off, washed with water, and then dissolved in boiling water, in which it is difficultly soluble. On cooling, the salt was deposited in long, white, lustrous needles, which when dry are not changed by light. If a solution of the salt be allowed to stand in the light, it becomes faintly opalescent after a time. The salt contains no water of crystallisation.

I. 0.2817 gram air-dried salt gave 0.1041 gram Ag.
II. 0.2685 gram air-dried salt gave 0.0998 gram Ag.
III. 0.2258 gram air-dried salt gave 0.0840 gram Ag.

	Calculated.		Found.		
			I.	II.	III.
$C_7H_4SO_3N$	182	62.76	...	...	...
Ag	108	37.24	36.95	37.17	37.20

The silver was determined by heating the salt in the air and afterwards in a current of hydrogen.

Barium anhydro-sulphamine-benzoate,

$\left[C_6H_4<\substack{CO\\SO_2}>N\right]_2Ba + 1\frac{1}{2}H_2O$.—The barium salt was prepared by adding pure barium carbonate to a hot solution of the sulphinide. It is easily soluble in water. From the concentrated solution it is deposited in botryoidal masses. Several attempts were made to obtain it in better form, but without success. If a few drops of the solution containing the salt be slowly evaporated on a glass plate, beautiful radiating needles are formed. After separating the salt from the mother-liquor, it was washed with absolute alcohol and dried in the air. The salt loses weight at 180°, but loses nothing above this.

0.2633 gram air-dried salt lost 0.0265 gram H_2O at 180°.

	Calculated for $(C_7H_4SNO_3)_2Ba + 3H_2O$.	Found.
$3H_2O$	9.69	10.06

I. 0.2368 gram anhydrous salt gave 0.1143 gram $BaSO_4$.
II. 0.2310 gram anhydrous salt gave 0.1118 gram $BaSO_4$.

	Calculated.		Found.	
			I.	II.
$(C_7H_4SNO_3)_2$	364	72.65	...	...
Ba	137	27.35	28.17	28.02
	501	100.00		

The results are not satisfactory, but still they are nearer to those required by the composition assumed than they are to those required by a salt derived from the sulphamine acid $C_6H_4{<}\begin{smallmatrix}COOH\\SO_2NH_2\end{smallmatrix}$. When this salt was first described[1] the results obtained pointed to the formula $\left[C_6H_4{<}\begin{smallmatrix}COO\\SO_2NH_2\end{smallmatrix}\right]_2Ba$. It seems probable that the salt undergoes slight decomposition when its solutions are evaporated.

Attempts to Prepare Ethereal Salts of Benzoic Sulphinide.

Although Remsen and Fahlberg state[1] that phosphorus pentachloride does not act upon benzoic sulphinide, it was thought desirable, in view of the results subsequently obtained by Remsen and Stokes,[2] to study this reaction somewhat more carefully. Accordingly four grams of the sulphinide and an equal weight of phosphorus pentachloride were thoroughly mixed and gently heated over a free flame. The entire mass became liquid. After cooling, methyl alcohol was poured upon the semi-solid material, but apparently no action took place. On warming, the substance dissolved. Water was added, and the excess of alcohol distilled off. On cooling, about a gram of benzoic sulphinide was deposited. On further evaporation a deposit of short, fine needles was obtained, which, after two crystallisations, were obtained in long, delicate, curved needles, which branched off from one another and arranged themselves concentrically in bunches. They were found to melt at 123°–125°.

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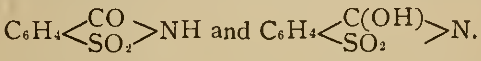
[1] This Journal **1**, 431.

[2] *Ibid.* **6**, 260.

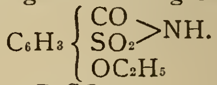
Three grams of the silver salt of the sulphinide were next placed in a small bottle closed by means of a ground-glass plate which could be clamped tightly down, and an excess of methyl iodide added. This was heated on a water-bath at about 100° for six hours. The formation of silver iodide was noticed soon after the heating began. The contents of the bottle were finally treated with hot alcohol, the silver iodide filtered off, the filtrate diluted with water and heated to drive off the alcohol. On cooling there separated from this solution delicate, curved, somewhat flattened needles, grouped together concentrically, which resembled the substance above described, obtained by treating the sulphinide with phosphorus pentachloride and methyl alcohol. The new substance melted at first at 116°–119°, but after two recrystallisations the fusing-point rose to 128°–129°. Owing to a lack of time and material the question whether the two substances here referred to are identical or not was, for the present, left unanswered. The ethereal salts of the sulphinide are now under investigation by Mr. R. N. Brackett, and the results will be published during the next academic year. It is hoped that by a careful investigation of these compounds it will be possible to decide between the two most probable formulas for the sulphinide—viz.:



$$C_6H_4<\begin{matrix}CO\\SO_2\end{matrix}>NH \text{ and } C_6H_4<\begin{matrix}C(OH)\\SO_2\end{matrix}>N.$$

III.—ON PARA-ETHOXY-BENZOIC SULPHINIDE.

By Ira Remsen and A. G. Palmer.

The ethoxy-toluene-sulphamide which formed the starting-point in the experiments described in this paper was made as will be described in another communication.[1] The oxidation was effected thus: 10 grams of the sulphamide were put in two litres of water, 20 grams of potassium permanganate added, and the whole heated on a water-bath. The operation required about six hours for its completion. A slight excess of permanganate was destroyed by the addition of a few cubic centimetres of alcohol. The solution was filtered from the oxides of manganese and evaporated to about 300 cc. On adding hydrochloric acid the sulphinide separated in fine white needles. These were recrystallised from water, and thus obtained in long, delicate, curved needles grouped together concentrically. The substance melts at 257°–258° (uncorrected), at the same time undergoing partial decomposition. Sulphur and nitrogen estimations were made, and gave results agreeing closely with those required for the formula  $C_6H_3\left\{\begin{array}{l}\left.\begin{array}{l}CO\\SO_2\end{array}\right>NH.\\OC_2H_5\end{array}\right.$

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[1] See page 243.

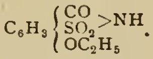
I. 0.2455 gram substance gave 0.2511 gram $BaSO_4$.

II. 0.2375 gram substance gave 0.2472 gram $BaSO_4$.

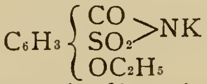
III. 0.2293 gram substance gave 0.2362 gram $BaSO_4$.

IV. 0.221 gram substance gave NH_3, which neutralised 2.75 cc. standard acid (1 cc. = 0.01778 gram H_2SO_4).

V. 0.2016 gram substance gave NH_3, which neutralised 2.46 cc. of the same standard acid.

Calculated for  $C_6H_3\left\{\begin{array}{l}\left.\begin{array}{l}CO\\SO_2\end{array}\right>NH.\\OC_2H_5\end{array}\right.$			Found.				
			I.	II.	III.	IV.	V.
$C_9H_5O_4$	181	79.74	...	...	...	...	...
S	32	14.09	14.04	14.21	14.15	...	...
N	14	6.17	...	...	...	6.27	6.14
		100.00					

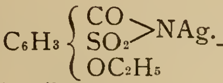
The substitution of the ethoxyl group for hydrogen destroys the marked sweet taste which is so characteristic of benzoic sulphinide.

Potassium salt,  $C_6H_3\left\{\begin{array}{l}\left.\begin{array}{l}CO\\SO_2\end{array}\right>NK\\OC_2H_5\end{array}\right.$.—This was made in the same way as the potassium salt of benzoic sulphinide. It is slightly less soluble than the latter. When a solution of the salt is slowly evaporated on the water-bath until it shows signs of crystallising, and then allowed to cool, the crystallisation will start from a point, and, in a few minutes, long, white, curved, silken needles will grow out and fill the whole solution. These crystals were collected on a filter, washed with strong alcohol, dried in the air and analysed. The air-dried salt lost slightly in weight at 100°, but suffered no loss above this.

I. 0.2482 gram substance dried at 100° gave 0.0799 gram K_2SO_4.

II. 0.3346 gram substance dried at 100° gave 0.1093 gram K_2SO_4.

	Calculated.		Found.	
			I.	II.
$C_9H_8SNO_4$	226	85.28	...	...
K	39	14.72	14.45	14.66
	265	100.00		

Silver salt, 
$C_6H_3\left\{\begin{array}{l}CO\\SO_2\\OC_2H_5\end{array}\right.\!\!>NAg.$—This salt was prepared in the same way as the silver salt of benzoic sulphinide, which it closely resembles. It is, however, more difficultly soluble in water. From solutions which are not too concentrated it crystallises in delicate, lustrous needles.

I. 0.2902 gram substance gave 0.0930 gram Ag.
II. 0.3247 gram substance gave 0.1042 gram Ag.

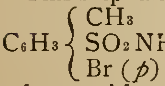
	Calculated.		Found.	
			I.	II.
$C_9H_8SNO_4$	226	67.66	...	...
Ag	108	32.34	32.05	32.03

The barium and calcium salts were made, but as they could not be obtained in well-defined forms, they were not analysed.

With phosphorus pentachloride and methyl alcohol, ethoxybenzoic sulphinide yields a product which crystallises well, and melts at 148°–149°. This has not as yet been examined further.

IV.—ON PARA-BROM-BENZOIC SULPHINIDE.

By Ira Remsen and W. S. Bayley.

This sulphinide was made by oxidising brom-toluene-sulphamide, 
$C_6H_3\left\{\begin{array}{l}CH_3\\SO_2NH_2\ (o)\\Br\ (p)\end{array}\right.$, which was obtained by treating para-brom-toluene with concentrated sulphuric acid, and by the usual reactions transforming the sulphonic acid into the corresponding amide.[1] The amide had all the properties ascribed to it by Hübner and Post. The oxidation was effected by boiling with a solution of potassium permanganate. As the yield obtained in the first experiments fell far short of the theoretical, several experiments were made for the purpose of determining the best conditions for the oxidation. In each experiment 20 grams of sulphamide were

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[1] See Hübner and Post, Annalen der Chemie **169**, 21.

used. The products were treated in the same way and purified to the same extent.

No. of Experiment.	$KMnO_4$ used.	KOH used.
1	30 grams	0 grams
2	45	0
3	30	10
4	45	10
5	60	0
6	60	10

In Experiment 1 a considerable quantity of unoxidised sulphamide and about 0.2 gram sulphinide were obtained.

In Experiment 3 a small quantity of unoxidised substance and about 0.3 gram sulphinide were obtained.

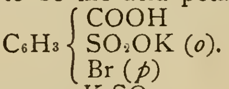
In Experiments 2 and 4 a larger quantity of the sulphinide was formed, and no unoxidised material remained.

In Experiment 5 the yield of sulphinide was 0.880 gram, and in Experiment 6 it was 1.400 gram.

It thus appears that the best results are obtained when a strongly alkaline solution is used, and a considerable excess of permanganate.

After filtering off the crystallised sulphinide the filtrate was examined for further products. During the oxidation ammonia was given off, and it was therefore clear that a part of the sulphamide must have suffered some change other than the oxidation of the methyl. The filtrate was evaporated to dryness and then extracted with hot alcohol. The solution thus obtained was allowed to cool, when brilliant scales with pearly lustre and beautiful iridescence separated.

This was examined and found to be the acid potassium salt of para-brom-sulpho-benzoic acid,[1]



$$C_6H_3\begin{cases}COOH\\ SO_2OK\ (o).\\ Br\ (p)\end{cases}$$

I. 0.3008 gram salt gave 0.0813 gram K_2SO_4.

II. 0.1510 gram salt gave 0.0406 gram K_2SO_4.

III. 0.2850 gram salt gave 0.2155 gram $BaSO_4$ (Liebig's method for the estimation of sulphur modified by Keiser).

	Calculated.	Found.		
		I.	II.	III.
K	12.25	12.13	12.10	...
S	10.03	...	...	10.38

---

[1] Annalen der Chemie **169**, 26.

This acid potassium salt is very soluble in water and difficultly soluble in alcohol. When treated successively with phosphorus pentachloride and ammonia it yields the sulphinide.

The yield of this salt was greatest in Experiments 2 and 5 of the series above described. Experiment 2 gave about 3 grams; Experiment 5 gave 2.02 grams; and Experiment 6 gave 0.5 gram. It follows, therefore, that the best total yield of sulphinide is obtained by using an excess of permanganate, without the addition of caustic potash.

Para-brom-benzoic sulphinide crystallises in long needles, a little thicker than those of the sulphamide. It is easily soluble in alcohol and in hot water, but difficultly soluble in cold water, and almost insoluble in hydrochloric acid. It is volatile at about 200°, and sublimes in feathery flakes. Its most remarkable property is its taste. *When first placed on the tongue its taste is extremely sweet*, fully as much so as that of benzoic sulphinide, a single small crystal being sufficient to sweeten a half litre of water. *After the sweet taste has passed, an equally bitter taste takes its place*, reminding one in its extreme bitterness of that of strychnine. This peculiarity cannot be due to the presence of two substances of different degrees of solubility, as the purest specimens, after the most careful purification, had the same property.[1]

The sulphinide melts at 217° (uncorrected).

Analyses were made with the results recorded below.

I. 0.29035 gram sulphinide gave 0.2571 gram $BaSO_4$ (Liebig's method for sulphur).

II. 0.3528 gram sulphinide gave 0.3145 gram $BaSO_4$.

	Theoretical for $C_7H_4O_3SNBr$.	Found.	
		I.	II.
S	12.21	12.17	12.25

A determination of nitrogen made by Mr. Talmage gave 5.72 per cent., while the theoretical percentage is 5.34.

Barium salt, $(C_7H_3O_3SNBr)_2Ba + 7\frac{1}{2}H_2O$.

I. 0.2372 gram salt lost 0.0360 gram at 185°.

II. 0.4060 gram salt lost 0.0606 gram at 185°.

III. 0.2372 gram salt lost 0.0351 gram at 145°.

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[1] This substance has since been investigated from a physiological standpoint by Dr. W. H. Howell and Mr. J. H. Kastle, of this University, and the results will soon be published elsewhere.

IV. 0.2707 gram salt lost 0.0403 gram at 145°.
V. 0.3064 gram salt lost 0.0451 gram at 145°.

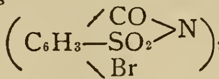
	Theoretical for $(C_7H_3O_3SNBr)_2Ba + 7\frac{1}{2}H_2O$.	Found.				
		I.	II.	III.	IV.	V.
H_2O	15.09	15.18	14.90	14.80	14.84	14.72

I. 0.2309 gram anhydrous salt gave 0.0817 gram $BaSO_4$.
II. 0.2613 gram anhydrous salt gave 0.0903 gram $BaSO_4$.
III. 0.2012 gram anhydrous salt gave 0.0713 gram $BaSO_4$.

	Theoretical for $(C_7H_3O_3SNBr)_2Ba$.	Found.		
		I.	II.	III.
Ba	20.79	20.85	20.32	20.88

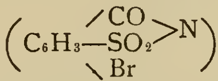
The salt was made by neutralising the free acid with pure barium carbonate and crystallising the resulting compound, when it was obtained in tufts of very fine, silky fibres, with a soft, downy appearance. It is not easily soluble in cold water, but easily in hot water. It is very sweet, and slightly less bitter than the free acid.

From the analyses given above it follows that the salt is represented by the formula



$$\left(C_6H_3{-}\begin{array}{l}\diagup CO\\ SO_2\\ \diagdown Br\end{array}\!\!>N\right)_2Ba.$$

Calcium salt,



$$\left(C_6H_3{-}\begin{array}{l}\diagup CO\\ SO_2\\ \diagdown Br\end{array}\!\!>N\right)_2Ca + 7\tfrac{1}{2}H_2O.$$

—This salt was made by neutralising the free acid with calcium carbonate. It has a sweetish taste, with but little bitterness. It crystallises in stellar aggregates. It is somewhat more soluble than the barium salt.

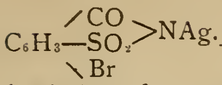
The analyses gave the results recorded below.

I. 0.5844 gram salt lost 0.1048 gram at 200°.
II. 0.2823 gram salt lost 0.0501 gram at 205°.
III. 0.2984 gram salt lost 0.0525 gram at 205°.

	Theoretical for $(C_7H_3O_3SNBr)_2Ca + 7\frac{1}{2}H_2O$.	Found.		
		I.	II.	III.
H_2O	17.23	17.93	17.74	17.59

I. 0.4796 gram anhydrous salt gave 0.1173 gram $CaSO_4$.
II. 0.2460 gram anhydrous salt gave 0.0592 gram $CaSO_4$.
III. 0.2322 gram anhydrous salt gave 0.0562 gram $CaSO_4$.

	Theoretical for $(C_7H_3O_3SNBr)_2Ca$.	Found.		
		I.	II.	III.
Ca	7.12	7.19	7.12	7.01



$C_6H_3\begin{cases} CO \\ SO_2 \\ Br \end{cases}$, with CO and SO_2 $>NAg$

Silver salt, $C_6H_3(Br)\langle^{CO}_{SO_2}\rangle NAg$.—This was made by precipitating an ammoniacal solution of the sulphinide with silver nitrate. It falls as a white, curdy precipitate, insoluble in cold water, difficultly soluble in hot water, from which it crystallises in very short, fine needles. It has a sweet taste, and turns violet on standing in the light.

After drying, the salt was burned in oxygen and then in hydrogen.

I. 0.2207 gram salt lost 0.0024 gram at 190°.

II. 0.2611 gram salt lost 0.0028 gram at 180°.

	Theoretical for $C_7H_3O_3SNBrAg + 2\frac{1}{2}H_2O$.	Found.	
		I.	II.
H_2O	1.08	1.09	1.07

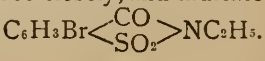
I. 0.2183 gram anhydrous salt gave 0.0633 gram Ag.

	Theoretical for $C_7H_3O_3SNBrAg$.	Found.
Ag	29.27	28.96

A neutralisation experiment with phenol-phthaleïn as an indicator showed that there is but one acid hydrogen atom in the sulphinide.

Action of Phosphorus Pentachloride and Alcohol.

About 0.7 gram sulphinide was treated with phosphorus pentachloride. No action took place until the mixture was heated. Hydrochloric acid was given off for a short time, and then the action stopped. On heating somewhat higher a further evolution of the gas took place, the whole mass becoming crystalline. After cooling, this was treated with absolute alcohol. A brown solution was thus formed, and a white residue left behind. The residue proved to be very difficultly soluble in alcohol and ether, and almost insoluble in water. It was dissolved in hot alcohol, from which, on cooling, it separated in the form of slightly yellowish crystals having the appearance of flat rhombs and feathery aggregates. They melted at 199°–199.5° (uncorrected). Saponified with caustic potash the substance yielded the sulphinide. It was insoluble in hydrochloric acid and potassium carbonate, and, consequently, had neither acid nor basic properties. Three sulphur estimations were made. These agree closely, and indicate that the substance is the mono-ethyl ester $C_6H_3Br\langle^{CO}_{SO_2}\rangle NC_2H_5$.



$C_6H_3Br\langle^{CO}_{SO_2}\rangle NC_2H_5$

I. 0.2927 gram substance gave 0.2322 gram $BaSO_4$.
II. 0.4805 gram substance gave 0.3789 gram $BaSO_4$.
III. 0.4185 gram substance gave 0.3262 gram $BaSO_4$.

	Calculated for $C_7H_3BrO_3SNC_2H_5$.	Found.		
		I.	II.	III.
S	11.04	10.90	10.84	10.71

An attempt was made to make the ethyl ester of the sulphinide by treating the silver salt with ethyl iodide. It was a matter of importance to determine whether the product of this reaction is identical with that obtained by treating the sulphinide successively with phosphorus pentachloride and alcohol. If the sulphinide has the structure indicated by the formula $C_6H_3Br{<}\substack{C(OH)\\SO_2}{>}N$, then the ethereal salts obtained from it by treating it with phosphorus pentachloride and alcohol, and by treating the silver salt with ethyl iodide, ought, apparently, to be identical. The reactions which we we would expect are, first, the formation of the chloride $C_6H_3Br{<}\substack{CCl\\SO_2}{>}N$, and from this, by treatment with alcohol, there would be formed the ethereal salt, $C_6H_3Br{<}\substack{COC_2H_5\\SO_2}{>}N$. And in the case of the silver salt the reactions would consist, first, in the formation of the salt $C_6H_3Br{<}\substack{COAg\\SO_2}{>}N$, and, second, in the formation of the ethereal salt $C_6H_3Br{<}\substack{COC_2H_5\\SO_2}{>}N$. On the other hand, if the formula $C_6H_3Br{<}\substack{CO\\SO_2}{>}NH$ represents the structure of the sulphinide, then the reaction with phosphorus pentachloride would probably take place in two stages:

I. $C_6H_3Br{<}\substack{CO\\SO_2}{>}NH + PCl_5 = C_6H_3Br{<}\substack{CCl_2\\SO_2}{>}NH + POCl_3$.

II. $C_6H_3Br{<}\substack{CCl_2\\SO_2}{>}NH = C_6H_3Br{<}\substack{CCl\\SO_2}{>}N + HCl$.

From the chloride obtained as the final product of the two reactions the ethereal salt $C_6H_3Br{<}\substack{COC_2H_5\\SO_2}{>}N$ would be formed. While the ethereal salt formed from the silver salt $C_6H_3Br{<}\substack{CO\\SO_2}{>}NAg$ would have the formula $C_6H_3Br{<}\substack{CO\\SO_2}{>}NC_2H_5$, and would therefore not be identical with the one obtained by treating the sulphinide successively with phosphorus pentachloride and alcohol.

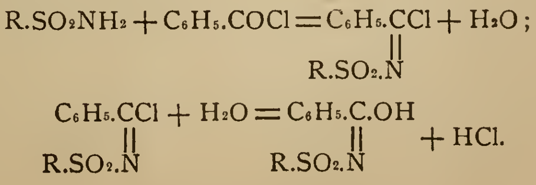
About 5 grams of the dried silver salt were treated with ethyl iodide in a closed bottle. The resulting compound was treated with absolute alcohol, and a part of it thus dissolved. That which dissolved was precipitated by water. It was found to melt at 185°. That which remained undissolved was dissolved in hot water, and was obtained from the solution in very long, delicate needles, which were very difficultly soluble in cold water, but easily soluble in hot water. They fused at about 125°. The substances were so impure that no positive conclusion can be drawn from the experiments just described. It is, however, certain that at least two products are formed when the silver salt of sulphinide is treated with ethyl iodide, and the principal product is not identical with that which is obtained by treating the sulphinide with phosphorus pentachloride and alcohol.

V.—ON BENZOYL-TOLUENE-SULPHAMIDE AND SOME OF ITS DERIVATIVES.

By Ira Remsen and C. S. Palmer.

The similarity in structure between the sulphinides and the compounds of the general formula $\begin{matrix} R.SO_2 \\ R.CO \end{matrix}{>}NH$, in which R represents a hydrocarbon residue, made it desirable to learn more regarding the conduct of the latter compounds. Accordingly the investigation here described was undertaken.

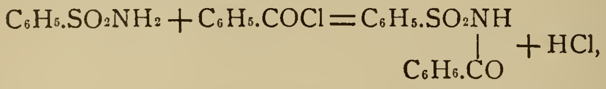
Among the best known compounds of the class referred to are those obtained from the sulphamides of benzene and toluene by treatment with benzoyl chloride. They are represented by the formulas $\begin{matrix} C_6H_5.SO_2 \\ C_6H_5.CO \end{matrix}{>}NH$ and $\begin{matrix} CH_3.C_6H_4.SO_2 \\ C_6H_5.CO \end{matrix}{>}NH$, and are known respectively by the names benzoyl-benzene-sulphamide and benzoyl-toluene-sulphamide. While the above formulas have not been seriously questioned, it must be remembered that they are open to some doubt, for it is quite possible that the reaction between the sulphamide and benzoyl chloride takes place as represented in these equations :



$$R.SO_2NH_2 + C_6H_5.COCl = \begin{array}{c} C_6H_5.CCl \\ \| \\ R.SO_2.N \end{array} + H_2O\,;$$

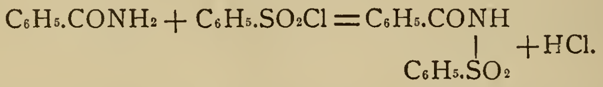
$$\begin{array}{c} C_6H_5.CCl \\ \| \\ R.SO_2.N \end{array} + H_2O = \begin{array}{c} C_6H_5.C.OH \\ \| \\ R.SO_2.N \end{array} + HCl.$$

Without further evidence than has thus far been presented, it is impossible to decide between the two views. There is, indeed, one fact which appears rather to favor the view just put forward. If the reaction between benzene-sulphamide and benzoyl chloride takes place as represented by the equation—



$$C_6H_5.SO_2NH_2 + C_6H_5.COCl = \begin{array}{r} C_6H_5.SO_2NH \\ | \\ C_6H_6.CO \end{array} + HCl,$$

then it is difficult to see why, when benzamide is treated with benzene-sulpho-chloride, the same product should not be obtained, thus:



$$C_6H_5.CONH_2 + C_6H_5.SO_2Cl = \begin{array}{r} C_6H_5.CONH \\ | \\ C_6H_5.SO_2 \end{array} + HCl.$$

The formulas of the products of these two reactions are identical, and the kind of action involved is the same. As a matter of fact, however, Wolkow[1] has shown that, when toluene-sulpho-chloride and benzamide act upon each other, reaction takes place in an entirely different way, the result being expressed by the equation:

$$C_7H_7SO_2Cl + C_6H_5.CONH_2 = C_7H_7SO_3H + HCl + C_6H_5CN.$$

We have repeated the experiment and obtained the same result. It is difficult to explain this if we assume that, in the action of benzoyl chloride upon benzene-sulphamide, the chlorine of the chloride unites directly with one hydrogen of the amide group. If, on the other hand, we assume that the first thing which takes place in the case just mentioned is the union of the two hydrogen atoms of the amide group with the oxygen of the carbonyl, and that this water subsequently acts upon the chloride thus formed, then it is possible to understand why, when toluene-sulpho-chloride acts upon benzamide, the products should be different from those obtained by the action of benzoyl chloride upon toluene-sulphamide. It is quite possible that under the influence of the sulpho-chloride, which acts as a dehydrating agent, benzamide may give up water and thus yield phenyl cyanide. The water would then act upon the sulpho-chloride, forming free sulphonic acid and hydrochloric acid. The reaction between toluene-sulphamide and benzoyl chloride would, according to this view, be represented thus:

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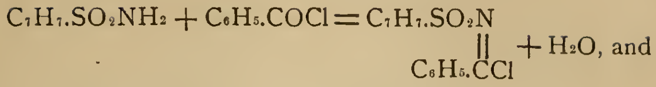
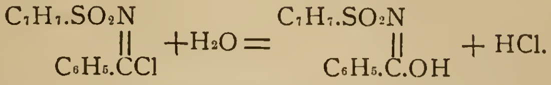
[1] Zeitschrift für Chemie, 1871, 421.



$$C_7H_7.SO_2NH_2 + C_6H_5.COCl = \begin{array}{c} C_7H_7.SO_2N \\ \| \\ C_6H_5.CCl \end{array} + H_2O, \text{ and}$$



$$\begin{array}{c} C_7H_7.SO_2N \\ \| \\ C_6H_5.CCl \end{array} + H_2O = \begin{array}{c} C_7H_7.SO_2N \\ \| \\ C_6H_5.C.OH \end{array} + HCl.$$

While the reaction between toluene-sulpho-chloride and benzamide would be represented thus:

$$C_7H_7.SO_2Cl + C_6H_5.CONH_2 = C_6H_5CN + H_2O + C_7H_7.SO_2Cl,$$
$$\text{and } C_7H_7.SO_2Cl + H_2O = C_7H_7.SO_2OH + HCl.$$

As will be seen, the reactions in the two cases are analogous. In the first case the amide hydrogen atoms combine with a carbonyl oxygen in another molecule. In the second case the same reaction takes place within the molecule of benzamide.

Theoretically, the simplest way to decide between the two views regarding the structure of the benzoyl derivatives of the sulphamides consists in studying the ethereal salts. If the structure is represented by the general formula $\begin{matrix} R.SO_2 \\ R.CO \end{matrix}\!>\!NH$, then the ethereal salts obtained by treating the compounds successively with phosphorus pentachloride and alcohols should have the general structure $\begin{matrix} R.SO_2 \\ \\ R.C.OR \end{matrix}\!>\!N$, while those obtained by treating the silver or lead salts with alkyl iodides should have the structure $\begin{matrix} R.SO_2 \\ R.CO \end{matrix}\!>\!NR$. On the other hand, if the compounds have the structure $\begin{matrix} R.SO_2 \\ \\ R.C.OH \end{matrix}\!>\!N$, then, whether the ethereal salts are made by one or the other of the methods, they must have the structure $\begin{matrix} R.SO_2 \\ \\ R.C.OR \end{matrix}\!>\!N$.

According to Gerhardt,[1] Wolkow[2] and Wallach,[3] when benzoyltoluene-sulphamide is treated with phosphorus pentachloride, a chloride is formed which, when treated with water or with alcohol, yields the original benzoyl sulphamide. Thinking that by changing the conditions it might be possible to get an ester from the chloride, we repeated the experiment, but we found that the chloride easily passes back into the benzoyl compound when treated with alcohol, and we were unable to make the reaction take any other course. The reaction is represented by the equation—

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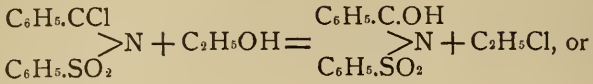
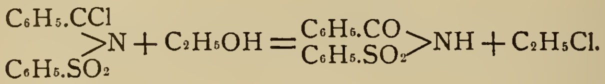
[1] Annalen der Chemie **108**, 214.

[2] Berichte d. deutsch. chem. Gesell. **2**, 137.

[3] Annalen der Chemie **214**, 193.

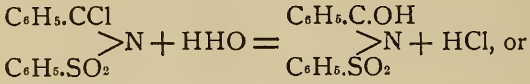


$$\begin{matrix}C_6H_5.CCl\\ C_6H_5.SO_2\end{matrix}{>}N + C_2H_5OH = \begin{matrix}C_6H_5.C.OH\\ C_6H_5.SO_2\end{matrix}{>}N + C_2H_5Cl, \text{ or}$$

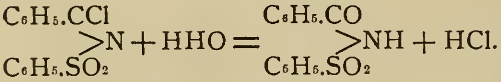


$$\begin{matrix}C_6H_5.CCl\\ C_6H_5.SO_2\end{matrix}{>}N + C_2H_5OH = \begin{matrix}C_6H_5.CO\\ C_6H_5.SO_2\end{matrix}{>}NH + C_2H_5Cl.$$

When treated with water also the chloride yields the original benzoyl compound, and the reaction does not take place as readily as with alcohol. Continued boiling is necessary to complete the transformation. The reaction is represented thus:



$$\begin{matrix}C_6H_5.CCl\\ C_6H_5.SO_2\end{matrix}{>}N + HHO = \begin{matrix}C_6H_5.C.OH\\ C_6H_5.SO_2\end{matrix}{>}N + HCl, \text{ or}$$



$$\begin{matrix}C_6H_5.CCl\\ C_6H_5.SO_2\end{matrix}{>}N + HHO = \begin{matrix}C_6H_5.CO\\ C_6H_5.SO_2\end{matrix}{>}NH + HCl.$$

It will be seen that these reactions are more readily understood on the hypothesis that the *lactim condition*, $—N=\underset{|}{C}.OH$, exists in the benzoyl compound, than they are on the hypothesis that the *lactam condition*, $\underset{|}{\overset{\overset{O}{\|}}{C}}—NH$, exists in the compound. Further, it is clear that the condition represented by the formula $—N=\underset{|}{C}—OR$, is one not easily attained.

Attempts to Prepare Esters of Benzoyl-benzene-sulphamide from the Salts.

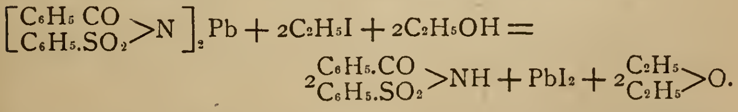
The silver salt of benzoyl-benzene-sulphamide was made by precipitating an ammoniacal solution of the benzoyl compound with silver nitrate. It was dried at 120° for several hours. Between four and five grams were enclosed with the equivalent quantity of ethyl iodide, and a small quantity of 99 per cent. alcohol in a Lintner's flask. This was immersed in a bath of boiling water for some days. Reaction began almost at once, as was shown by change of color, but the heating was continued until the reaction appeared to be complete. In subsequent experiments the lead salt was used instead of the silver salt, with apparently equally good results. It was prepared by treating an ammoniacal solution of the benzoyl compound with lead acetate. It forms a white, amorphous precipitate, which is almost completely insoluble in water. Two determinations of lead were made, which gave respectively 41.33 and 41.45 per cent. A salt of the composition $\left[\begin{matrix}C_6H_5.SO_2\\C_6H_5.CO\end{matrix}>N\right]_2Pb$ contains 41.63 per cent. lead.

This salt was treated as above described, in order to transform it into the ethyl ester. A substance was obtained which, after repeated crystallisations from alcohol, melted at 141° (uncorr.). This is the melting-point of the original benzoyl compound. The other properties of the substance also indicated that the product of the reaction is nothing but the original compound. Finally, analyses were made which removed all doubt.

	Calculated for $C_{13}H_{11}NO_3S$.	Found. I.	Found. II.
S	12.26	12.55	12.64
N	5.36	5.46	5.76

The fact is thus established that when the lead salt of benzoyl-benzene-sulphamide is treated with ethyl iodide and alcohol under the conditions above described, benzoyl-benzene-sulphamide is formed, together with lead iodide. It is difficult to see how ethyl iodide alone acting upon the lead salt could give the results obtained, and it was therefore suspected that the alcohol took part in the reaction. To test this, some of the dried lead salt was mixed with dry ethyl iodide, and dry benzene was used as the menstruum. This mixture was heated for several days, but no indication of reaction was observed. The pressure flask was opened and a very little water added. On now heating again the reaction took place without difficulty; lead iodide and the benzoyl compound being the products.

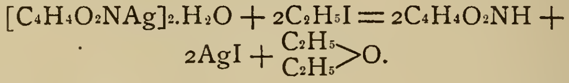
As to what takes place when alcohol is used as the menstruum, the simplest suggestion is that represented by this equation:



$$\left[\begin{matrix}C_6H_5\,CO\\C_6H_5.SO_2\end{matrix}>N\right]_2Pb + 2C_2H_5I + 2C_2H_5OH =$$
$$2\begin{matrix}C_6H_5.CO\\C_6H_5.SO_2\end{matrix}>NH + PbI_2 + 2\begin{matrix}C_2H_5\\C_2H_5\end{matrix}>O.$$

According to this, ethyl ether ought to be found among the products of the reaction. On subjecting the liquid contents of the flask to fractional distillation a small quantity of ether was separated in pure condition. Its boiling-point and odor left no doubt as to its identity.

Similar ineffectual attempts to obtain esters by treating the lead or silver salts of so-called imides with alkyl iodides have been made by others. Menschutkin[1] tried to make the ethyl ester of succinimide by treating the silver salt with ethyl iodide. Instead of getting the ester he got the original succinimide. He represents the reaction by the equation—



$$[C_4H_4O_2NAg]_2.H_2O + 2C_2H_5I = 2C_4H_4O_2NH + 2AgI + {C_2H_5 \atop C_2H_5}{>}O.$$

He does not appear to have proved the formation of ether.

In repeating the work of Menschutkin, Lansberg[2] got the same result, but he further proved that ether is formed in the reaction. In attempting to make the ethyl ester of phthalimide by treating the silver salt with ethyl iodide, Lansberg[3] obtained only the imide itself. He tried the use of reagents free from water, and states that the reaction takes place as usual. In view of the result obtained by us when dry reagents were used, this statement of Lansberg needs verification.

The substances which we commonly call acids are such as readily give up hydrogen and take up metals in its place, and we associate with this the power which acids possess of yielding neutral compounds by taking up hydrocarbon residues in the place of the acid hydrogen. In the complex compounds with which we are dealing, and of which benzoyl-benzene-sulphamide is a good example, it appears that we have a class of substances which form salts but do not form esters, or at least they do not form esters by the common reaction. They are acid with reference to metallic bases, but not with reference to alcoholic substances. It is not improbable that this is true for most so-called acid imides. Whether it is true for the sulphinides or not appears doubtful. Some results obtained by Stokes and Remsen,[4] and by Bayley and Remsen,[5] seem to indicate that it is not. It will be the object of future investigations to show in how far the acid imides, such as succinimide, phthalimide, etc.; the di-acid imides, such as

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[1] Annalen der Chemie **162**, 165.

[2] *Ibid.* **215**, 172.

[3] *Loc. cit.*

[4] This Journal **6**, 260.

[5] See p. 234 *ante*.

$\begin{matrix}\mathrm{R.CO}\\ \mathrm{R.CO}\end{matrix}\!>\mathrm{NH}$, $\begin{matrix}\mathrm{R.SO_2}\\ \mathrm{R.CO}\end{matrix}\!>\mathrm{NH}$, etc.; and the sulphinides, $\mathrm{R}<\begin{matrix}\mathrm{CO}\\ \mathrm{SO_2}\end{matrix}>\mathrm{NH}$, are analogous substances.

Preparation of Compounds of the General Formula $\begin{matrix}\mathrm{R.SO_2}\\ \mathrm{R.CO}\end{matrix}\!>\mathrm{NR}$.

Having shown that it is extremely difficult, if not impossible, to introduce hydrocarbon residues into benzoyl-benzene-sulphamide, it became an interesting question whether it is possible to prepare substances of the general formula $\begin{matrix}\mathrm{R.SO_2}\\ \mathrm{R.CO}\end{matrix}\!>\mathrm{NR}$. If the benzoyl compound is a lactam—*i. e.*, if it contains the grouping $\underset{\mathrm{CO}}{>}\mathrm{NH}—$ then a compound of the above formula must be regarded as an ester. If, on the other hand, the benzoyl compound is a lactim, containing the grouping $—\mathrm{N}=\mathrm{C(OH)}$, then a compound of the above formula would not be a derivative of the benzoyl sulphamide.

In order to prepare the compounds, substituted sulphamides were first made, such as $\mathrm{C_7H_7.SO_2NHCH_3}$, $\mathrm{C_7H_7.SO_2NHC_2H_5}$ and $\mathrm{C_7H_7.SO_2NHC_6H_5}$, and these were treated with benzoyl chloride.

Methyl-para-toluene-sulphamide, $\mathrm{C_7H_7.SO_2.NH.CH_3}$. — This compound was made by treating pure para-toluene-sulpho-chloride with the necessary quantity of a 33 per cent. solution of methyl amine. Reaction took place at once, with considerable evolution of heat. In order to insure complete transformation the temperature of a water-bath was maintained for two hours. The result was a brownish oil, which became white on being repeatedly washed with water, and then solidified. It is extremely easily soluble in alcohol, apparently mixing with it in all proportions. When hot water is added to the alcoholic solution, and the whole allowed to stand, the compound crystallises out in rectangular plates which melt at 75°. It can also be crystallised from hot water alone, in which it is slightly soluble. It has no acid properties, and is very stable.

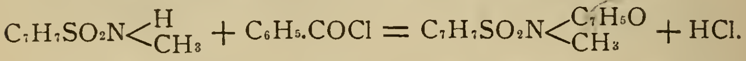
	Calculated for $\mathrm{C_8H_{11}NO_2S}$.	Found.
S	17.27	17.12
N	7.56	7.80

Ethyl-para-toluene-sulphamide, $\mathrm{C_7H_7.SO_2.NH.C_2H_5}$.—This was prepared from toluene-sulpho-chloride and ethyl amine similarly to the methyl compound just described. The compound treated in the same way as the methyl compound formed rectangular plates melting at 58°.

	Calculated for $C_9H_{13}NO_2S$.	Found.
S	16.08	16.43
N	7.33	7.80

Phenyl-para-toluene-sulphamide, $C_7H_7.SO_2.NH.C_6H_5$. — This compound was first made by Müller from toluene-sulpho-chloride and aniline. Crystallised from alcohol, in which it is easily soluble, it melts at 103°. No difficulty was encountered in preparing it.

Benzoyl-methyl-toluene-sulphamide, $C_7H_7SO_2N<^{CH_3}_{C_7H_5O}$.—This was prepared from the methyl amide above described by mixing it with an equivalent quantity of benzoyl chloride and heating in an oil-bath at 140° for three hours. Hydrochloric acid was given off, and in all probability the reaction took place thus:



$$C_7H_7SO_2N<^{H}_{CH_3} + C_6H_5.COCl = C_7H_7SO_2N<^{C_7H_5O}_{CH_3} + HCl.$$

The product was a brownish oil, which became almost colorless on washing with water. After standing for some time a solution in alcohol and water deposits crystals, though in some cases such a mixture forms an emulsion from which even after long standing no crystals are deposited. The crystals melt at 58°, and appear to be asymmetric.

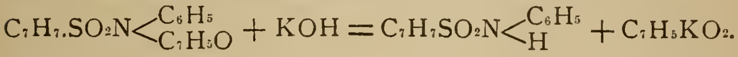
	Calculated for $C_{15}H_{15}NO_3S$.	Found.	
		I.	II.
S	11.41	11.50	11.20
N	4.86	4.96	5.00

Benzoyl-ethyl-toluene-sulphamide, $C_7H_7.SO_2N<^{C_2H_5}_{C_7H_5O}$. — Reaction takes place between benzoyl chloride and ethyl-toluene-sulpho-chloride as readily as in the case just described. The product crystallises less easily than the corresponding methyl compound. After long standing a few crystals made their appearance, but the substance was not analysed.

Benzoyl-phenyl-toluene-sulphamide, $C_7H_7.SO_2N<^{C_6H_5}_{C_7H_5O}$.—The anilid melting at 103° (see above) was treated with benzoyl chloride in an oil-bath at 140° for three hours. Hydrochloric acid is given off. The product is easily crystallised from alcohol. It crystallises in square tables or plates, or lathe-shaped crystals. It melts at 149° (corrected).

	Calculated for $C_{20}H_{17}NO_3S$.	Found.	
		I.	II.
S	9.13	9.30	9.50
N	3.97	3.96[1]	3.82[1]

This compound, like the other benzoyl compounds described in this paper, is a stable substance. When boiled with an alcoholic solution of caustic potash it breaks down, yielding benzoic acid and toluene-sulphanilide, according to the equation—



$$C_7H_7.SO_2N\left<\begin{matrix}C_6H_5\\C_7H_5O\end{matrix}\right. + KOH = C_7H_7SO_2N\left<\begin{matrix}C_6H_5\\H\end{matrix}\right. + C_7H_5KO_2.$$

ON THE DECOMPOSITION OF DIAZO-COMPOUNDS.

I.—ON THE CONDUCT OF PARA-DIAZO-ORTHO-TOLUENE-SULPHONIC ACID TOWARDS ALCOHOL.

By Ira Remsen and A. G. Palmer.

The work described in this paper was originally undertaken for the purpose of perfecting a more convenient method for the preparation of benzoic sulphinide, $C_6H_4\left<\begin{matrix}CO\\SO_2\end{matrix}\right>NH$, than that now in use. It was proposed to treat para-nitro-toluene with sulphuric acid, thus making the sulphonic acid, $C_6H_3\begin{matrix}\diagup CH_3\\ —SO_3H\ (o)\\ \diagdown NO_2\ (p)\end{matrix}$, and then, by converting this nitro-compound into the amido-compound with a reducing agent, making the diazo-compound, and boiling this with alcohol, to pass to ortho-toluene-sulphonic acid. The hope of success was based largely upon the statements of Jensen[2] to the effect that he had accomplished the transformations it was proposed to effect. A few years before Jensen's paper appeared, Ascher[3] had transformed the diazo-compound of para-amido-ortho-toluene-sulphonic acid into ortho-toluene-sulphonic acid by boiling with alcohol under a pressure corresponding to 300 mm.

[1] The nitrogen was determined by Mr. J. H. Holmes by the method of Kjehldahl.

[2] Annalen der Chemie **172**, 235. [3] *Ibid.* **161**, 8.

of mercury in addition to the atmospheric pressure. Neither of these authors refers to any difficulties encountered in his work.

The preparation of amido-toluene-sulphonic acid is a simple matter and requires no special precautions. In making the nitro-sulphonic acid we found the directions of Beilstein and Kuhlberg[1] to be in every way satisfactory. The calcium salt first obtained was converted into the potassium salt, which crystallises in beautiful long needles, and can be easily purified. The reduction of the salt to the corresponding amido-compound was effected by dissolving in strong ammonia and saturating with hydrogen sulphide. The solution became of a dark reddish color. It was heated on the water-bath to drive off the excess of ammonium sulphide, and finally evaporated to dryness. Water was then added, the precipitated sulphur filtered off, and hydrochloric acid added to the filtrate, when para-amido-ortho-toluene-sulphonic acid was thrown down in the form of hard, glistening rhombohedral crystals.[2] The acid was easily purified by crystallisation from water. Those portions which are deposited from the mother-liquors are contaminated with sulphur, and the perfect separation of the two substances is by no means a simple matter.

The diazo-compound was prepared as follows: The amido-acid was very finely powdered. This was found to be of the highest importance. The more finely it is powdered the more easily is the diazo-compound formed. The amido-compound was brought into a flask with from five to ten parts of absolute alcohol, and a rapid current of nitrogen trioxide (from arsenious oxide and nitric acid) passed in. The flask should be surrounded with cold water, and should be thoroughly shaken at frequent intervals. When the substance in suspension has assumed a coarsely granular appearance, and settles quickly to the bottom after it has been shaken up, leaving a perfectly clear solution, the operation should be stopped, for if the oxides of nitrogen be conducted into the liquid after this point is reached, it begins to assume a reddish color, and the solid matter grows dark in color. The diazo-compound is now quickly filtered off and thoroughly washed with alcohol, and then kept covered with absolute alcohol, in which condition it undergoes no change even if kept for a considerable time. When dried and exposed to the air the compound turns brown, and is evidently decomposed. It dissolves readily in water, forming a deep red solution.

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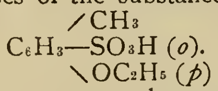
[1] Annalen der Chemie **155**, 8.

[2] Experiments since carried on in this laboratory by Messrs. Hayes and Brackett have shown that the reduction can be better effected by means of tin and hydrochloric acid. The details will be given later.—I. R.

As the decomposition of the diazo-compound with alcohol can be effected only by the aid of considerable pressure, an apparatus was devised of such construction as to permit the maintenance of a constant pressure for any length of time, and the escape of the gaseous products of the decomposition. A round-bottomed strong flask of the capacity of one litre is covered with a tightly woven netting of copper wire. This is fitted with a rubber stopper with two holes. Through one of these passes a glass tube which connects with an open end manometer; through the other passes a brass tube which leads to a simple safety-valve. The valve is of the kind commonly used in steam-boilers. It is provided with a carefully ground, accurately fitting conical valve, a lever and an adjustable weight. The manometer is constructed of such dimensions that it will register a pressure of 800 mm. of mercury, and it is provided with a scale divided into spaces of ten mm. each. It will be seen that by this means any desired pressure up to 800 mm. could be maintained. The reaction was started in the flask while the safety-valve was closed. The rise of the mercury in the manometer showed the pressure, and when the desired pressure was reached the weight on the lever of the valve was so placed as to allow the valve to open at that pressure. The apparatus worked satisfactorily in every way, and was used in all the experiments to be described. As much as 50 grams of the diazo-compound can be decomposed in one operation without any risk of explosion.

In the first experiment performed 100 grams of the diazo-compound were decomposed in two portions under a pressure of 300 mm. Both nitrogen and aldehyde were given off. After all action had ceased the excess of alcohol was distilled off, and there remained a dark, reddish syrupy liquid which was strongly acid. This was diluted with water and neutralised with barium carbonate. It was attempted to purify the barium salt by recrystallisation, but it was found impossible to separate it entirely from the dark, gummy impurity which it contained, and it was therefore converted into the sodium salt, and this transformed by the action of phosphorus pentachloride and ammonia into the amide. This, as at first obtained, was a dark, spongy, sticky mass. When treated with hot water it melted to a dark oil. It was digested with large quantities of hot water, but there remained at last an insoluble black tar. The aqueous extracts were united and evaporated down, when a somewhat colored, semi-crystalline mass was deposited. This was collected and recrystallised from hot water, bone-black being used to remove the color. After crystallisation from a mixture of one part of alcohol and three parts of water it was obtained in the form of long, flattened, white, lustrous needles, which melted constantly at 143°–144° (uncorr.). This melting-point was not changed by further recrystallisations. The amide of ortho-toluene-sulphonic acid which was looked for as the product melts at 153°–154°. To make it absolutely certain that the substance actually obtained was not impure ortho-toluene-sulphamide, it was recrystallised twelve times from alcohol and water; but this did not change the melting-point perceptibly. A small portion of the amide was now oxidised with a solution of potassium permanganate. If it were ortho-toluene-sulphamide, it must have yielded benzoic sulphinide, which could be easily recognised by its sweet taste and other characteristic properties. After heating for some time on the water-bath, although the permanganate was reduced, no indication of the formation of benzoic sulphinide was obtained. Analyses of the substance showed it to be *ethoxy-toluene-sulphamide*,



$$C_6H_3\begin{array}{l}\diagup CH_3\\ —SO_3H\ (o).\\ \diagdown OC_2H_5\ (p)\end{array}$$

I. 0.3423 gram substance gave 0.3690 gram $BaSO_4$.

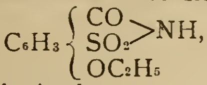
II. 0.3048 gram substance gave 0.3316 gram $BaSO_4$.

III. 0.2671 gram substance gave 0.2913 gram $BaSO_4$.

IV. 0.2658 gram substance gave NH_3, which required for neutralisation 3.4 cc. standard acid: 1 cc. = 0.01778 gram H_2SO_4.

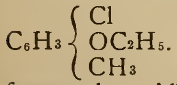
V. 0.2510 gram substance gave NH_3, which required for neutralisation 3.27 cc. of the same standard acid.

	Calculated for $C_6H_3\begin{cases}CH_3\\ SO_3H.\\ OC_2H_5\end{cases}$	Found.				
		I.	II.	III.	IV.	V.
S	14.88	14.80	14.94	14.97	...	...
N	6.51	...	...	...	6.49	6.69

As was mentioned above, aldehyde was given off in the decomposition of the diazo-compound, and it therefore appeared probable that, to some extent at least, reaction must have taken place as stated by Jensen and Ascher. A careful examination of the mother-liquors showed that they contained a small quantity of ortho-toluene-sulphamide, although it was not separated in pure condition. Its presence was proved by oxidising the impure products. In this way, together with a considerable quantity of ethoxy-benzoic sulphinide,  $C_6H_3\left\{\begin{array}{l}\left.\begin{array}{l}CO\\SO_2\end{array}\right>NH,\\OC_2H_5\end{array}\right.$ a small quantity of benzoic sulphinide was obtained.

Although the experiment just described was far from satisfactory, it showed conclusively that when diazo-toluene-sulphamide is decomposed by boiling with alcohol under the conditions mentioned by Jensen and by Ascher, the chief reaction is that which yields the ethoxy-compound, and not, as was assumed by these chemists, that which yields the toluene-sulphamide.

A number of observations of a similar kind have been made, but thus far it has been found to be impossible to furnish any satisfactory explanation of the reaction. As is well known, it is at present assumed by all writers that the normal reaction of diazo-compounds when boiled with alcohol is that which results in the replacement of the diazo-group by hydrogen. It is, however, certain that the reaction frequently takes place in such a way as to form phenetols. From experiments which have been carried on by Mr. W. R. Orndorff in this laboratory it appears probable that the *normal* reaction is the one which gives the phenetol. Certain it is that when the sulphate or nitrate of diazo-benzene nitrate is boiled with alcohol the quantity of benzene formed is extremely small, while a very considerable quantity of phenetol, $C_6H_5.O.C_2H_5$, is formed. These experiments are still in progress, and the results obtained will be described hereafter.

The first recorded observation of the formation of ethers by decomposition of diazo-compounds with alcohol is that described by Wroblewsky.[1] He found that two chlor-toluidines which he was investigating, when converted into the diazo-compounds and boiled with alcohol, gave the corresponding chlor-phenetols,  $C_6H_3\left\{\begin{array}{l}Cl\\OC_2H_5.\\CH_3\end{array}\right.$ After this, similar observations were made quite frequently. All that are described in the literature are here mentioned, as the subject has recently attracted considerable attention, and no one seems to have brought all the observations together as yet.

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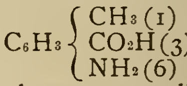
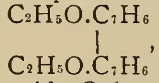
[1] Zeitschrift für Chemie **6**, 164; Berichte **3**, 98.

Fittica[1] states that his fourth variety of nitro-benzoic acid (yellow nitro-benzoic acid), when converted into the amido-acid and diazo-compound, yields ethoxy-benzoic acid when boiled with alcohol. Hayduck[2] effected the same transformation in the case of ortho-amido-para-toluene-sulphonic acid. Zander[3] showed that amido-benzene-disulphonic acid gives the ethoxy-compound. In this case a pressure of 400 mm. was needed to effect the decomposition. W. Balentine[4] endeavored to decompose the diazo-compound of hydrazo-benzene-sulphonic acid by heating with absolute alcohol under a pressure of 400 mm. He says: "The decomposition proceeded very slowly with the evolution of nitrogen, but the odor of aldehyde was not perceptible, as it is in the case of other diazo-compounds." The product of this decomposition does not appear to have been examined. Paysan[5] obtained ethoxy-para-toluene-sulphamide from ortho-amido-para-toluene-sulphamide. Mohr,[6] on making the diazo-compound from para-amido-benzyl-sulphonic acid, found that with alcohol under a pressure of 360 mm. ethoxy-benzyl-sulphonic acid is formed. Heffter[7] studied the action of alcohol on the diazo-compound from *para-amido-ortho-toluene-sulphinic acid*, and obtained *ethoxy-toluene-sulphonic acid.* The author describes the amide of this acid as a crystallised substance melting at 136°. As we have shown, however, this compound melts at 143°–144°. Whether Heffter really had ethoxy-ortho-toluene-sulphonic acid in his hands or not it is impossible to decide on the evidence. It is certainly difficult to understand how he got a sulphonic acid from a sulphinic acid by the method adopted. Attention was first called to the reaction in this laboratory by an observation made by Broun[8] to the effect that when the diazo-compound from amido-toluic acid,  $C_6H_3\left\{\begin{array}{l}CH_3\,(1)\\ CO_2H\,(3)\\ NH_2\,(6)\end{array}\right.$, is treated with alcohol it yields quantitatively the corresponding ethoxy-compound. Schulz[9] obtained from toluidine, diethoxy-ditolyl,  $\begin{array}{c}C_2H_5O.C_7H_6\\ |\\ C_2H_5O.C_7H_6\end{array}$, and a similar derivative from amido-ethyl-benzoic acid. Quite recently Haller[10] and Hofmann[11] have published papers on this subject. Haller found that, when the sulphate of the diazo-compound from crystallised cumidine is heated with alcohol under a pressure of 200 mm. of mercury, a compound of the formula $C_6H_2(CH_3)_3.OC_2H_5$ is formed. The same author showed that reaction takes place in the same way with the sulphate of diazo-phenetol and of β-diazo-naphthalene. Hofmann effected a similar transformation of tetra-methyl-amido-benzene.

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[1] Berichte d. deutsch. chem. Gesell. **6**, 1209.
[2] Annalen der Chemie **172**, 215.
[3] *Ibid.* **198**, 1.
[4] *Ibid.* **202**, 351.
[5] *Ibid.* **221**, 210.
[6] *Ibid.* **221**, 220.
[7] *Ibid.* **221**, 351.
[8] This Journal **4**, 374.
[9] Berichte d. deutsch. chem. Gesell. **17**, 468.
[10] *Ibid.* **17**, 1887.
[11] *Ibid.* **17**, 1917.

From the examples cited above it will be seen that substances differing widely from one another in character undergo this peculiar transformation, and there is no common feature presented by all of them which suggests an explanation.

Influence of Pressure on the Course of the Reaction.

The fact that pressure is necessary in several of the cases cited, and that, in the case studied by us, two products are formed—ortho-toluene-sulphamide and the ethoxy-compound—suggested that by varying the pressure the proportions of the two substances formed might be varied, so that a conclusion could be drawn as to whether increased pressure favors the formation of the ethoxy-compound or *vice versa.*

I. A quantity of the diazo-compound was heated with absolute alcohol under a pressure of 120 mm. The decomposition took place more quietly and slowly than under 300 mm. pressure. It was accompanied by the evolution of nitrogen and aldehyde. The resulting sulphonic acids were converted into the sodium salts, and these in turn into the corresponding sulphamides. These were oxidised, and the quantities of benzoic sulphinide and the ethoxy-derivative obtained determined. As nearly as could be estimated the quantity of ortho-toluene-sulphonic acid formed in the reaction with alcohol was to that of the ethoxy-toluene-sulphonic acid as one to three.

II. Under a pressure of 150 mm. the results obtained were about the same as those described in the preceding paragraph.

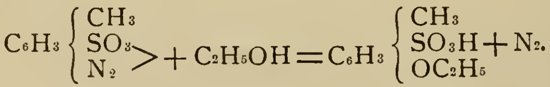
III. As has already been stated, when a pressure of 300 mm. is employed, the proportion of toluene-sulphonic acid to the ethoxy-compound is very small, certainly much smaller than in Experiments I and II.

IV. Finally an experiment was made in which a pressure of 500 mm. was employed. In this experiment 80 grams of the diazo-compound were decomposed, 20 grams being used at once. The decomposition took place rapidly, and was complete in about four minutes. The odor of aldehyde was not perceptible in the escaping gases. The acid residue in this case was not nearly as dark as in the preceding experiments. It was converted as before into the sulphamides, which were obtained in better form than in the other experiments. The product of the oxidation was almost wholly ethoxy-sulphinide. The mother-liquors were sweet, showing that some of the benzoic sulphinide was present, but, although careful search was made for it, it was not present in sufficient quantity to make its separation in crystalline form possible. It appears, therefore, that, when the diazo-compound is decomposed with alcohol under a pressure of 500 mm., the main reaction which takes place is that which results in the formation of the ethoxy-compound.

V. The lowest pressure at which the decomposition could be effected was 90 mm. At this pressure the reaction was far from clear, the yield being highly unsatisfactory. From 250 grams of the amido-acid there were obtained 45 grams of the ethoxy-sulphamide and 47 grams of the ortho-toluene-sulphamide. This shows, at least, that at this pressure the yield of toluene-sulphonic acid is greater in proportion to that of the ethoxy-compound than in any of the other experiments.

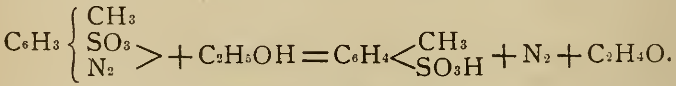
The experiments above described show that the higher the pressure the larger the proportion of ethoxy-compound formed and the lower the pressure the larger the proportion of toluene-sulphonic acid formed.

Under high pressure the reaction takes place as represented in this equation :



$$C_6H_3\left\{\begin{array}{l}CH_3\\ \left.\begin{array}{l}SO_3\\ N_2\end{array}\right>\end{array}\right. + C_2H_5OH = C_6H_3\left\{\begin{array}{l}CH_3\\ SO_3H\\ OC_2H_5\end{array}\right. + N_2.$$

While at low pressure it takes place according to this equation :



$$C_6H_3\left\{\begin{array}{l}CH_3\\ \left.\begin{array}{l}SO_3\\ N_2\end{array}\right>\end{array}\right. + C_2H_5OH = C_6H_4\left<\begin{array}{l}CH_3\\ SO_3H\end{array}\right. + N_2 + C_2H_4O.$$

It is too early to offer any suggestion as to the reason why pressure causes the result here recorded. It is highly desirable that further experiments on the influence of pressure on the reaction between diazo-compounds and alcohol should be undertaken, with the view of determining whether the influence in other cases is the same as that observed in the case under discussion. It is intended in time to continue this investigation.

An attempt was made to get ortho-sulpho-benzoic acid by first oxidising nitro-toluene-sulphonic acid to nitro-sulpho-benzoic, then reducing this, and, after converting the amido-acid into the diazo-compound, treating this with alcohol. The diazo-compound, however, proved to be even less easily decomposed than the one used in the above experiments. It was finally placed in a sealed vessel and heated in a water-bath, but even this did not decompose it.

METHODS FOR DETERMINING THE RELATIVE STABILITY OF THE ALKYL BROMIDES.

By Ira Remsen and H. W. Hillyer.

A careful study of the relative ease with which bromine can be extracted from the alkyl bromides by different reagents would undoubtedly reveal many facts of interest and importance. Unfortunately, such a study is extremely difficult, owing to a variety of circumstances. In the first place, the bromides of the lower members of the series are quite volatile, and, if allowed to stand at the ordinary temperature, the quantity of substance under experiment constantly decreases. In the second place, the bromides are not soluble in water, a fact which makes it difficult to apply reagents which are insoluble in alcohol. Again, the method which first suggests itself—viz.: reduction by means of nascent hydrogen—is one which it is extremely difficult to apply quantitatively. Notwithstanding these and other obstacles, it was thought desirable to make a preliminary study of the different methods which suggested themselves, with the view of determining which of the methods are most promising, and what the general character of the results obtained is. These results cannot lay claim to great accuracy, but, as will be seen, they are interesting as showing the relative stability of the bromides which were investigated. The bromides experimented upon were those at hand: ethyl bromide, normal and isopropyl bromides, butyl bromide and amyl bromide (boiling-point 119°).

Action of Zinc and Sulphuric Acid.

The first experiments which yielded results of interest were those in which the reducing agent was hydrogen from zinc and sulphuric acid. A solution containing 75 cc. of equal parts of alcohol of about 94 per cent., and of sulphuric acid of about 10 per cent., and a quantity of bromide, such that it contained 200 milligrams of bromine, was placed in an Erlenmeyer flask of 125 cc. capacity. The zinc used was the common sheet zinc, cut in pieces of one inch by one-half inch. These were bent in the middle at a right angle, so that, when resting upon the two ends, they would expose as uniform an extent of surface as possible. They were cleaned and slightly etched with dilute sulphuric acid, then washed and placed in the flasks, four in each flask, by means of a platinum wire hook, or, better, a small, tapering glass rod bent at a right angle near the end.

The extent of the reduction was determined by estimating by Volhard's method the quantity of bromine abstracted. It was soon discovered that the nitrate of silver decomposed the bromides to a considerable extent, so that in the later experiments the method used consisted in adding ferric sulphate and a small quantity of sulpho-cyanate solution, and then titrating to disappearance of color, thus leaving the nitrate as short a time as possible in contact with the bromide. The titrating solutions were so made that each cubic centimetre was equivalent to one milligram of bromine.

In this way ethyl, isopropyl and butyl bromides were first examined. It was found that a larger percentage of alcohol was necessary for the solution of the amyl bromide, so that, in a second series, in which isopropyl, amyl and normal propyl bromides were examined, the solvent was 50 cc. alcohol and 40 cc. acid. The figures indicate the total number of milligrams of bromine abstracted from the bromides. This is true also of all subsequent tables given in this paper. All of the experiments of shorter duration described in this paper were carried on in flasks surrounded by flowing water of 9° or 10° temperature. The flasks in the other experiments were also put in water, but the flow of water was not kept up, so that the temperature varied slightly with the temperature of the laboratory. In the first series of experiments, the results of which are recorded below, the time of action was two and a half hours.

SERIES I.

Experiment 1	Butyl, 3·9	Ethyl not measurable.
" 2	" 3·9	" 0.7 (?)
" 3	" 3·9	" 6 and 1.2.
" 4	" 3·3	Isopropyl, 10.6 and 8.4.
" 5	" 3·3	" 9.6 " 7.8.

It will be seen that the five experiments with butyl bromide gave results which agreed fairly well with one another, a fact which shows that the method is worthy of consideration. In the four experiments with ethyl bromide the results varied from a quantity of bromine which was too small to be determined to 1.2 milligrams. Finally, in the case of isopropyl bromide, the quantities of bromine extracted in the four cases varied from 7.8 to 10.6. While these results are not as satisfactory as could be desired, they clearly show the relative ease with which the three bromides experimented upon are decomposed by the reagent used. Leaving out the first experiment with ethyl bromide, it appears that, under the same conditions, hydrogen from zinc and sulphuric acid extracts from four to five times as much bromine from butyl bromide as it does from ethyl bromide, and about three times as much from isopropyl bromide as from butyl bromide.

SERIES II.

Experiment 1	Isopropyl, 6.7	Amyl, 3.2 and 3.2.
" 2	" 5·9	N. propyl, .7 " .7.

The time in these experiments was not as long as in the first series.

The results show that the amyl bromide used is somewhat more easily decomposed than normal butyl bromide, and that normal propyl bromide has approximately the same stability as ethyl bromide. The order of stability towards nascent hydrogen evolved from zinc and sulphuric acid is, beginning with the most stable: Ethyl, normal propyl, normal butyl, amyl (from fermentation alcohol) and isopropyl bromide. The most important general statement to which the results lead is that *the bromides of primary alcohols decrease in stability towards zinc and sulphuric acid as we pass from the lower members of the series to the higher.*

The marked instability of isopropyl bromide, as compared with normal propyl bromide, indicates that the secondary bromides are much less stable than the corresponding normal bromides.

Another series of experiments confirmed the results already commented upon, as far as the order of stability is concerned.

Action of Nascent Hydrogen Evolved from an Alkaline Solution.

Some time ago, at the suggestion of one of us (R.), Mr. E. H. Keiser tried some experiments on the action of sodium amalgam on alcoholic solution of alkyl bromides. The results were later found to be untrustworthy, because the alkali alone was found to decompose the bromides, and, as no allowance had been made for the double action, it was impossible to decide how much of the total action to attribute to the alkali and how much to the hydrogen. The fact that when sodium amalgam is used the quantity of alkali in solution is constantly increasing throughout the experiments, and at a comparatively rapid rate, complicates the conditions of the experiments. Accordingly, another method for getting nascent hydrogen from an alkaline solution was desirable, and the following was devised:

It had been observed that when zinc is put into an ammoniacal solution of cobalt sulphate it soon becomes coated with a firm, glossy coating of cobalt, and that in this condition it gives a fairly good evolution of hydrogen when placed in a solution of caustic soda. The zincs were prepared by placing them in a shallow dish resting on their ends, and covering them with a strongly ammoniacal solution of cobalt sulphate containing one or two grams to the litre, and sufficient ammonium sulphate to keep the cobalt in solution as double sulphate. The zincs were allowed to remain in this for a short time, till there was quite a rapid evolution of hydrogen, when the solution was poured off and the zincs washed. They were rendered more active by treating them with very dilute sulphuric acid and washing them a second time with several changes of water.

In the first experiments a large number of zincs were treated at once with the cobalt solution with the object of making them of equal reducing power. The caustic soda solution was made from sodium by dissolving about 65 grams of metallic sodium in a litre of alcohol of about 75 per cent.

The solutions, when in action, contain 30 cc. alcohol, 20 cc. water, 10 cc. caustic soda solution, and a quantity of bromide containing 200 milligrams of bromine. The soda solution was added, by means of a pipette, as rapidly as possible to the different flasks making up a series for comparison. At the end of the action the zincs were removed in the order in which they had been introduced, thus securing a very nearly equal time for the action of the zincs in each flask. An equal quantity of nitric acid was then added to each flask, sufficient to neutralise the alkali. In order to have a control of the rate of action in each series there was one flask with ethyl bromide and no zincs and one with ethyl bromide and four zincs. Parallel with these was run a series containing eight other flasks with some other bromide, four with four zincs each, and four without zincs, with the object of determining the action due to the hydrogen, by subtracting from the total amount of bromine extracted the quantity extracted by the alkali alone in the flasks without zincs. The action continued for about sixteen hours.

FIRST DAY'S EXPERIMENTS.

	With Zn.	Without Zn.	Difference.
Ethyl,	46.2	28.7	17.5
Amyl,	17.8	4.9	
“	19.9	4.2	
“	19.2	4.5	
“	19.9	4.9	
Mean,	19.2	4.6	14.6

SECOND DAY'S EXPERIMENTS.

	With Zn.	Without Zn.	Difference.
Ethyl,	44.1	26.6	17.5
Butyl,	12.4	3.4	
“	12.4	3.1	
“	11.9	3.4	
“	12.9	3.4	
Mean,	12.4	3.3	9.1

THIRD DAY'S EXPERIMENTS.

	With Zn.	Without Zn.	Difference.
Ethyl,	42.0	26.4	15.6
Isopropyl,	13.7	3.5	
“	13.5	3.3	
“	14.0		
“	13.7		
Mean,	13.7	3.4	10.3

As the quantity of bromine extracted from ethyl bromide in the third day's experiments is smaller than in the experiments of the first and second days, it is probable that the figure for isopropyl bromide does not truly represent its stability as compared with the bromides used in the experiments of the first and second days. The proportion

$$15.6 : 17.5 :: 10.3 : x$$

ought to give a figure comparable with the 14.6 obtained for amyl bromide and 9.1 obtained for butyl bromide.

Two series of observations were now carried on, each series including ethyl, normal propyl, isopropyl, butyl and amyl bromides. The results obtained in each series are comparable with one another, but the results obtained in Series I are not comparable with those obtained in Series II, as the conditions were not exactly the same in the two.

	SERIES I.	SERIES II.	
Ethyl,	40.9	54.2	with zincs.
"	28.0	35.7	without zincs.
"	12.9	18.5	difference.
N. Propyl,	24.5	32.2	with zincs.
"	9.8	11.9	without zincs.
"	14.7	20.3	difference.
Isopropyl,	11.5	16.4	with zincs.
"	5.6	4.9	without zincs.
"	5.9	11.5	difference.
Butyl,	11.2	12.6	with zincs.
"	3.5	3.8	without zincs.
"	7.7	8.8	difference.
Amyl,	16.8	18.5	with zincs.
"	4.5	5.6	without zincs.
"	12.3	12.9	difference.

These results, as well as those recorded on page 255, show at least that, whether we consider the total action of the alkali and the hydrogen, the action of the hydrogen alone as shown by the differences, or the action of the alkali alone, the order of stability is entirely different in these experiments from that obtained in the experiments with zinc and sulphuric acid. *In acid solution ethyl and normal propyl bromides are most stable, and isopropyl bromide least so. In alkaline solutions, on the contrary, the reverse is true; that is to say, ethyl and normal propyl bromides are least stable, and isopropyl bromide is, of these three, the most stable.* The results are less striking as far as butyl and amyl bromides are concerned. These bromides appear to have about the same stability towards alkali alone as isopropyl bromide, very much greater than ethyl bromide. On the other hand, the presence of the zincs increases the decomposition to about the same extent in the case of amyl bromide as in that of ethyl bromide; while, in the case of butyl bromide, the increase is somewhat less.

Action of Ammonia on Normal and Isopropyl Bromides.

The marked differences between the stability of propyl bromide and that of isopropyl bromide led to the examination of their conduct towards other reagents than those used in the experiments already described. The first one used was ammonia. Standard solutions were made by dissolving 3.8437 grams of each bromide in 250 cc. alcohol. Each cubic centimetre of this solution contained 10 milligrams of bromine. The substances were weighed in tubes of about 8 by 180 mm. drawn out to a point. One of these, after a file-scratch was made on it near the point, was placed on the balance pan in an upright position in a small beaker. After weighing, weights amounting to 3.8437 grams were added to the other pan and enough of the bromide was run in, by means of a narrow glass tube drawn to a point and used as a pipette, to bring again to a balance. It is not difficult, after a little practice, to weigh in this manner to within a milligram. The point of the weighing tube being thrust into the mouth of a 250 cc. measuring flask, was broken off by pressing it against the inside of the neck of the flask. After the bromide had run out the tube was immediately rinsed out by pouring alcohol through it. The flask was then filled to the mark with alcohol, and after thorough mixing the contents were transferred to tightly stoppered bottles. To 20 cc. of each of the solutions 20 cc. of aqueous ammonia of 10 per cent. were added. At the end of about twenty hours the bromine extracted was found to be, in the case of normal propyl bromide, 25.4 milligrams in one flask and 29.2 milligrams in another; in the case of isopropyl bromide, 3.8, 4.2 and 5.0 milligrams in three flasks.

From these results it is clear that normal propyl bromide is much more rapidly decomposed by ammonia than isopropyl bromide. As shown by the experiments above recorded, caustic soda alone extracted 9.8 and 11.9 milligrams of bromine from normal propyl bromide, while in parallel experiments it extracted only 5.6 and 4.9 milligrams of bromine from isopropyl bromide.

Action of Alcoholic Sodium Hydroxide on the Alkyl Bromides.

By way of supplementing the experiments described above, in which the action of sodium hydroxide on the bromides was studied, a more extended series of similar experiments was now undertaken. In each flask there were placed 20 cc. bromide solution, containing in all 200 milligrams of bromine, 10 cc. alcohol, and 20 cc. caustic soda solution, made by the action of water on sodium amalgam, and containing about 10 per cent. sodium hydroxide.

Of the 200 milligrams of bromine in each flask the following quantities were extracted:

Ethyl, . . .	165.6	or	82.8 per cent.
" . . .	159.2	"	79.6
N. Propyl, . . .	130.5	"	65.2
I. Propyl, . . .	50.4	"	25.2
Butyl, . . .	31.2	"	15.6
" . . .	32.2	"	16.1
Amyl, . . .	65.8	"	32.9
" . . .	67.6	"	33.8

These results confirm those already obtained, and indicate clearly that fairly satisfactory results may be expected by a similar comparison of other alkyl bromides with reference to their stability towards caustic soda. The reaction which takes place with this reagent is in all probability represented by the equation—

$$C_nH_{2n+1}Br + C_2H_5OH + NaOH = C_nH_{2n+1}.O.C_2H_5 + KBr + H_2O.$$

That is, a mixed ether containing ethyl and the radical of the bromide used is formed in each case. In the above experiments the odor of common ether was unmistakable in the flask with ethyl bromide. In the flask with propyl bromide there was also a pleasant odor like that of common ether, and quite different from that of the bromide solution. An experiment was performed in which a larger but unknown quantity of normal propyl bromide was treated with caustic soda and alcohol. After standing a week or two the mixture was made neutral with nitric acid, and subjected to distillation, when a small quantity of a volatile liquid was obtained, which had an odor very much like that of common ether, and a density less than that of water. The quantity was so small that the boiling-point could not be determined. Several cases are known[1] in which mixed ethers have been formed by treating halogen derivatives of the hydrocarbons with alcoholic potash at an elevated temperature, but the reaction has not been supposed to take place as easily as we have found it at the ordinary temperature.

Action of Soluble Silver Salts on the Two Propyl Bromides.

Preliminary experiments having shown that silver nitrate slowly decomposes the bromides, its action on the two propyl bromides was next tried.

20 cc. normal propyl bromide solution, 5 cc. dilute nitric acid, and 25 cc. solution of nitrate of silver, containing silver equivalent to 25 milligrams bromine, were put in a flask and allowed to stand for 16 hours in a dimly lighted place. At the end of this time there were considerable opalescence and some deposition of silver bromide. By titration it was found that 2.7 milligrams of bromine had combined with silver. A similar mixture containing isopropyl bromide was found to have deposited a heavy, yellowish-white precipitate of silver bromide. On titration it was found that, of the 25 milligrams of bromine with which the silver added was capable of combining, 24.3 milligrams were thus combined.

From a solution containing 20 cc. bromide solution, and 20 cc. of a neutral solution of silver acetate, capable of precipitating 20.2 milligrams bromine, 19.2 and 19.2 milligrams bromine were found precipitated in two parallel experiments with the isobromide, while only 2.5 and 2.5 milligrams were precipitated in parallel experiments with the normal bromide.

The isopropyl bromide is decomposed much more readily by silver nitrate and by silver acetate than normal propyl bromide. Towards silver salts, therefore, these two bromides act in the same way that they do towards zinc and sulphuric acid.

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[1] Annales de Chimie et de Phys. (3) **12**, 302; Jahresbericht, 1850, 560; Philosophical Magazine (4) **14**, 186; Annalen der Chemie **92**, 351; Journal of (London) Chem. Society **19**, 358.

Action of Cobalt-zincs and Acetic Acid on Alkyl Bromides.

Mixtures were made containing 20 cc. bromide solution and 10 cc. acetic acid of ordinary strength. These were allowed to act for two hours and twenty minutes on six cobalt-zincs prepared as above described. In the case of the normal bromide 2.0 and 1.9 milligrams of bromine were set free in two different flasks. In the case of the isobromide the quantities of bromine set free were 8.0 and 8.1 milligrams. By adding sufficient nitric acid all of the red ferric acetate formed by adding the ferric sulphate may be changed to the colorless nitrate, so that the titration by Volhard's method presents no difficulties. The action of the mixture of alcohol and acetic acid on the cobalt-zincs gives a very regular evolution of hydrogen, which, though not rapid, may be continued for five or six hours before the zinc acetate begins to crystallise out.

The form of the zincs was now changed to that of a flat spiral, made by winding a strip of zinc one-half inch by twenty-four inches about a small core, then unwinding and loosening the coil till no two turns were in contact. The coil was placed in a beaker which contained the solution of the bromide to be reduced, and a small glass rod, so bent as as to make a support for the coil, thus ensuring free circulation.

In one series of experiments in which the action was kept up for about five hours, the normal bromide yielded 4.5 and 4.8 milligrams bromine, and the isobromide 20.0 and 20.1 milligrams bromine.

Finally, a series of experiments was made including the five bromides. For this purpose standard solutions were made containing equivalent weights of the bromides, so that 1 cc. of each solution contained the same number of milligrams of bromine, the concentration being the same as that of the propyl bromides—viz.: 20 cc. of each solution containing 200 mm. of bromine. The conditions as regards quantity of bromide, of alcohol and of acid were the same as in the last case. The zincs, however, were different. At the end of five hours, titration gave the following results:

Bromide.	Mgrm. Br set free. I.	Mgrm. Br set free. II.
Ethyl,	1.2	1.5
N. Propyl,	3.3	3.3
I. Propyl,	10.5	11.7
Butyl,	6.0	6.0
Amyl,	9.0	9.9

It was afterwards found that, by standing in alcoholic solution alone, butyl and amyl bromides are slightly decomposed, so that the above figures for these bromides are somewhat too large.

As was stated at the beginning of this paper, the object of the investigation was to determine which of the various methods which suggest themselves for the purpose of measuring the relative stability of the alkyl bromides are most likely to yield results of value. It seems that the action of zinc and acids is not capable of giving very reliable results, though the general tendency of the action can easily be determined. The action of zinc in alkaline solution is so complicated by the independent action of the alkali alone that it is of little value. In the same way the action of sodium amalgam is also complicated by the fact that the solution constantly grows more and more alkaline. On the other hand, the action of salts of silver on fairly concentrated solutions of the bromides promises good results, as does also the action of ammonia and of caustic soda alone. It is proposed, as soon as possible, to study the reactions with care, using as large a number of bromides as may be obtainable. Among experiments already performed by others, and having some relation to those described in this paper, the following should be mentioned:

Wislicenus,[1] by treating various haloid ethers with the sodium compounds of aceto-acetic ester, ethyl aceto-acetic ester, and malonic ester without external application of heat, found the order of stability of some alkyl bromides and iodides. In the order of increasing stability he placed the compounds experimented upon thus: Methyl iodide, ethyl iodide, primary propyl iodide, ethyl bromide, primary isobutyl iodide, primary propyl bromide, tertiary butyl bromide. Or, taking the iodides alone: Methyl, ethyl, primary propyl, isopropyl, isobutyl. This is the same order as that observed in the series of experiments with alcoholic caustic soda.

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[1] Annalen der Chemie **212**, 239.

Jackson[1] studied the relative stability of certain substituted benzyl bromides. By the action of a solution of sodium acetate in alcohol on the ortho-, meta- and para-brom-benzyl bromides at 100°, he found that the ortho-bromide is the most stable towards this reagent, the meta next, and the para the least stable.

ON THE OXIDATION OF SUBSTITUTION PRODUCTS OF AROMATIC HYDROCARBONS.

XVII.—OXIDATION BY MEANS OF POTASSIUM PERMANGANATE.

By Ira Remsen.

In 1878 I called attention to an interesting uniformity in the action of fusing caustic potash on substituted hydrocarbons. Mainly on the basis of experiments made by Jacobsen,[2] it was shown that caustic potash oxidises hydrocarbon residues situated in the ortho-position, thus exerting an action directly the opposite of that exerted by chromic acid. In many earlier experiments a marked difference in the action of chromic acid in acid solution, and of potassium permanganate in alkaline solution, had been observed, and it was supposed that the difference was largely due to the fact that the solution in the one case is acid and in the other alkaline. Later Remsen and Palmer[3] showed that, with potassium permanganate, ortho-toluene-sulphamide is oxidised much more easily than the para- or the meta-amide, while the reverse is true when chromic acid is used. Further, nitric acid had been shown to act in general like chromic acid, so that the following language seemed to be justified:[4] "As it is established with a fair degree of certainty that acid oxidising agents tend to transform para-groups and leave ortho-groups unchanged, and that alkaline oxidising agents tend to transform ortho-groups and leave para-groups unchanged . . ." At a later date R. Meyer[5] made a more positive statement

[1] This Journal **3**, 252

[2] Berichte der deutsch. chem. Gesell. **14**, 2091.

[3] This Journal **4**, 142.

[4] *Loc. cit.* 143.

[5] Einleitung in das Studium der aromatischen Verbindungen, 179; and Annalen der Chemie **220**, 16.

regarding these phenomena. He says: "Auf Grund der von ihm selbst und von anderen Chemikern gemachten Beobachtungen stellt er (Remsen) den folgenden Satz auf: Negative Atome oder Atomgruppen, welche sich in der Orthostellung gegen Kohlenwasserstoffreste im Benzolkern befinden, üben einen schützenden Einfluss auf diese Reste aus, wenn die Verbindungen mit sauren Oxydationsmitteln behandelt werden. Wirkt dagegen ein alkalisches Oxydationsmittel ein, so wird gerade umgekehrt der in Orthostellung befindliche Rest oxydirt." Some experiments of R. Meyer and Baur[1] on the oxidation of cymene-sulphonic acid with potassium permanganate appeared to lend support to this general statement. When oxidised with potassium permanganate cymene-sulphonic acid, $C_6H_3\left\{\begin{array}{l}CH_3\\ SO_3H\ (o)\\ C_3H_7\ (p)\end{array}\right.$, is converted into oxypropyl-sulpho-benzoic acid, $C_6H_3\left\{\begin{array}{l}COOH\\ SO_3H\ (o)\\ C_3H_7O\ (p)\end{array}\right.$, or, the methyl which is in the ortho-position with reference to the sulpho-group is oxidised to carboxyl, while the isopropyl group, $CH{<}^{CH_3}_{CH_3}$, is simply changed to the oxypropyl group, $C(OH){<}^{CH_3}_{CH_3}$, being otherwise apparently "protected." On the other hand, when the same cymene-sulphonic acid is oxidised with nitric acid, the product is sulpho-para-toluic acid, $C_6H_3\left\{\begin{array}{l}CH_3\\ SO_3H\ (o)\\ COOH\ (p)\end{array}\right.$. Meyer says in regard to this case: "Das Verhalten der Cymolsulfosäure kann . . . . als eine Bestätigung des Remsen'schen Satzes betrachtet werden."

According to Jacobsen,[2] when meta-xylene-sulphamide, $C_6H_3\left\{\begin{array}{l}SO_3H\\ CH_3\ (o)\\ CH_3\ (p)\end{array}\right.$, is treated with potassium permanganate the first product is the same sulphamine-toluic acid as is formed when the oxidation is effected by means of chromic acid—viz.: $C_6H_3\left\{\begin{array}{l}SO_3H\\ CH_3\ (o)\\ CO_2H\ (p)\end{array}\right.$. As this result appeared to be opposed to that obtained by R. Meyer and Baur, the experiment was repeated by Mr. D. T. Day at my request, and Jacobsen's statement was confirmed. Not a trace of the isomeric acid was obtained. It was thought that, possibly, the para-position of the hydrocarbon residues in the cymene-sulphonic acid might have something to do with the result obtained, and therefore some experiments on the action of potassium permanganate on para-xylene-sulphonic acid were tried. These gave the same result as meta-xylene-sulphamide, showing that, as far as the product is concerned, it is immaterial whether chromic acid or potassium permanganate is used. Similar results were obtained with para-xylene-sulphamide. Attention was now turned to the case of cymene-sulphonic acid. Dr. Riggs repeated the experiment of Meyer and Baur, and found their statements correct in every respect. Finally, Mr. Emerson tried the action of potassium permanganate on cymene itself, and succeeded in showing that the first product of the action is oxypropylbenzoic acid, $C_6H_3, \left\{ \begin{array}{l} COOH \\ C_3H_7O \end{array} \right.$. It is, however, well known that, when cymene is oxidised with chromic acid, the first product of the action is toluic acid. The difference between the conduct of cymene-sulphonic acid towards nitric acid and that towards potassium permanganate is therefore due not to the presence of the sulpho-group, but to the difference between the methyl and propyl groups, and the experiment of Meyer and Baur furnishes no evidence in favor of the generalisation with regard to the action of alkaline oxidising agents. What is true of fusing caustic potash is not true of an alkaline solution of potassium permanganate.

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[1] Annalen der Chemie **220**, 6.

[2] Berichte d. deutsch. chem. Gesellschaft **11**, 899.

Oxidation of Derivatives of Para-xylene with Potassium Permanganate.

By W. H. Emerson.

The para-xylene used in these experiments was obtained from Kahlbaum. It solidified almost completely when cooled below the melting-point of pure para-xylene. For the preparation of the sulphonic acid 50 cc. para-xylene were treated with an equal volume of fuming sulphuric acid. In a few minutes the whole was in solution. The excess of sulphuric acid was removed, and the sulphonic acid converted into the potassium salt, and the solution of the latter evaporated to dryness.

In a preliminary experiment 50 grams of the sulphonate were treated with 90 grams potassium permanganate dissolved in 2250 cc. water. The chief product obtained was sulpho-terephthalic acid, while some of the xylene-sulphonic acid remained unoxidised.

This showed that, if a monobasic acid was formed, it was attacked in preference to the sulphonate when a certain proportion between the quantities of the substances was reached. In subsequent experiments a smaller proportion of permanganate was used. Good results were obtained when the amount calculated to oxidise one methyl group was used. 82 grams of the sulphonate were added to a solution of 50 grams caustic potash in 800 cc. water. The oxidation was carried on in two three-litre flasks heated in the water-bath. The permanganate solution (40 grams to the litre) was added, 100 cc. at a time, each portion being allowed to become decolorised before another was added. At first the reduction of 100 cc. required about half an hour, but the time necessary increased gradually up to more than an hour. The total added was 2900 cc. The solution was filtered from the precipitated oxides of manganese, neutralised with sulphuric acid, and evaporated to dryness, and the organic salts extracted with 80 per cent. alcohol. The salt extracted was recrystallised, and it was found to consist of a mixture of the unoxidised salt and the product of oxidation. The mother-liquors were treated with hydrochloric acid, which threw down a heavy, flaky, white precipitate with a satiny lustre. This was filtered, dried and recrystallised, and then analysed:

	Calculated for $C_6H_3\left\{\begin{matrix}CH_3\\CO_2H\\SO_3K\end{matrix}\right. + 2H_2O.$	Found.
H_2O	12.42	12.42
K	15.39	15.15

The salt crystallised well from water in long, transparent needles.

A part of this salt was converted into the barium salt by treatment with barium chloride. The barium salt thus obtained crystallised well from water, in needles, and is more insoluble than the potassium salt. The analysis gave the following results:

	Calculated for $C_6H_3\left\{\begin{matrix}CH_3\\CO_2H\\SO_3Ba\end{matrix}\right. + 2\tfrac{1}{2}H_2O.$	Found.
H_2O	13.70	13.10
Ba	24.16	24.08

The dry salt is extremely hygroscopic, a fact which may account for the low result obtained in determining the water of crystallisation.

In order to determine which of the two sulpho-para-toluic acids had been formed, some of the potassium salt was fused with caustic potash. The mass, after cooling, was dissolved in water, acidified and extracted with ether. The ethereal extract, after distillation, left behind an acid which proved to be volatile with water vapor. It was distilled with steam for the purpose of purifying it and then examined. Its solution was not colored with ferric chloride. It fused at 201°–205°. The acid was evidently α-ortho-homo-meta-oxy-benzoic acid, $C_6H_3\left\{\begin{array}{l}CH_3\\ OH\,(o)\\ CO_2H\,(p)\end{array}\right.$. According to von Gerichten and Rossler this acid fuses at 206°–207°. The only other possibility was α-meta-homo-salicylic acid, which melts thirty degrees lower, and gives an intense red color with ferric chloride. From this it is clear that the oxidation product obtained was the acid $C_6H_3\left\{\begin{array}{l}CH_3\\ SO_3H\,(o)\\ CO_2H\,(p)\end{array}\right.$, or the same as that which is obtained when chromic acid is used.

After distillation of the ethereal extract with water vapor a residue was left which proved to be oxy-terephthalic acid.

The product of oxidation was carefully examined to see whether it might not contain the isomeric sulphonic acid, but its absence was clearly shown. Incidentally a heavy, difficultly soluble barium salt was obtained. This was found to crystallise well in large, transparent prisms. It proved to be nothing but primary barium sulpho-terephthalate, as shown by the analysis.

	Calculated for $C_6H_3\left\{\begin{array}{l}(CO_2H)_2\\ SO_3ba\end{array}\right. + H_2O$.	Found.
H_2O	12.55	12.42
Ba	21.84	21.88

Oxidation of Para-xylene Sulphamide.

The amide used melted at 147.8° (corrected). 10 grams were dissolved in caustic potash and water in the proportions given above, and the oxidation carried on in the same manner. 650 cc. of the permanganate solution were used. After filtering, the solution was acidified, when a precipitate came down. This was nearly insoluble in cold water, and crystallised beautifully. It melted at 270°, at the same time showing signs of decomposition. A portion of this product was fused with caustic potash, and the oxy-acid thus formed examined. It proved to be the same as that obtained from the sulphonate. It melted at 207°–208°.

In this case, then, as well as in that of the sulphonate, the methyl group which is oxidised is not that which is in the ortho-position, relatively, to the sulpho-group.

The mother-liquor from which the amine acid was precipitated gave, on further evaporation, a finely crystallised precipitate of needles. This was purified and analysed and shown to be the acid potassium salt of sulpho-terephthalic acid.

	Calculated for $C_6H_3\left\{\begin{matrix}(CO_2H)_2\\SO_3K\end{matrix}\right. + H_2O$.	Found.
H_2O	5.96	6.19
K	13.77	13.74

Oxidation of Cymene with Potassium Permanganate.

By W. H. Emerson.

The specimen of cymene used was distilled, and only that portion taken for experiment which passed over between 172°–173° (uncorr.). 37 grams of cymene were oxidised with a mixture of 22 grams caustic potash in 370 cc. water, and 2200 cc. permanganate solution containing 40 grams to the litre. The oxidation was carried on in two flasks immersed in boiling water and provided with reflux condensers. All the permanganate was added at once. The time required for complete decolorisation was about three days. The solutions were filtered, nearly neutralised, evaporated to a small volume, and the acids precipitated with hydrochloric acid. A preliminary experiment having shown that at least two acids had been formed, one of them being probably terephthalic acid, the mixture of acids was converted into the calcium salts, in the hope that the difficult solubility of the terephthalate would afford a ready means of separation. From the most insoluble calcium salt there was obtained an acid which was extremely difficultly soluble in water, amorphous, infusible, and generally showing the properties of terephthalic acid. From the more soluble portion of the calcium salts it was found to be impossible to get a substance with a constant sharp melting-point. Even after repeated recrystallisations the acid melted at 150°–155°. The melting-point, the appearance and other general properties of the acid indicated that it was *oxypropyl-benzoic acid.*

According to R. Meyer[1] this acid melts at 155°–156°. It was transformed into propenyl-benzoic acid, $C_6H_4\left\{\begin{matrix}COOH\\C_3H_5\end{matrix}\right.$, by boiling with dilute hydrochloric acid. The product obtained was more difficultly soluble in water than oxypropyl-benzoic acid, and melted at 159°–160°. R. Meyer gives the melting-point 160°–161°. Further, by boiling the propenyl-benzoic acid with strong hydrochloric acid for several hours, it was converted into the difficultly soluble isopropenyl-benzoic acid melting at 245°–260°.

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[1] Annalen der Chemie **219**, 248.

The acid was converted into the barium salt and the salt analysed.

	Calculated for $(C_{10}H_9O_2)_2Ba + H_2O$.	Found.
H_2O	3.94	3.77
Ba	29.60	29.82

The above-described observations show conclusively that when cymene is oxidised with potassium permanganate the first product of the action is oxypropyl-benzoic acid, and that further action of the permanganate results in the formation of terephthalic acid. These two products are, as nearly as could be judged, formed in about equal quantities. R. Meyer[1] states that the only product of the oxidation of cymene with potassium permanganate is terephthalic acid. Only the two products mentioned could be found. Since these results were obtained, and during the writing of this description, a paper by Widman and Bladin has appeared,[2] in which the same results are given.

NOTE ON THE OXIDATION OF MONO-NITRO-MESITYLENE.

By W. H. Emerson.

The single exception to the rule that negative groups protect from the action of chromic acid hydrocarbon residues which are in the ortho-position is offered by mesitylene-sulphamide. When this is oxidised it yields a sulphinide,[3] the oxidation taking place in one of the ortho-methyls and proceeding no further. This case has always seemed especially remarkable since it has been shown that when brom[1]- and chlor[2]-mesitylene are oxidised the ortho-methyls are protected, and only the para-methyls are oxidised. Further, the same rule appeared to hold good for nitro-mesitylene as pointed out by Schmitz,[3] since para-nitro-mesitylenic acid is obtained as a secondary product in the preparation of mono-nitro-mesitylene. The oxidation of nitro-mesitylene had, however, not been effected, and it was therefore considered desirable to make some experiments in this direction.

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[1] Berichte d. deutsch. chem. Gesell. **13**, 1498. [2] *Ibid.* **19**, 583. [3] This Journal **2**, 130.

Nitro-mesitylene was made according to the directions of Ladenburg.[4] Dinitro-mesitylene was first made. This was converted into nitro-mesidine by reduction with alcoholic ammonium sulphide, and the nitro-mesidine then converted into nitro-mesitylene through the diazo-compound. Fittig[5] had attempted this oxidation with the chromic acid mixture, but failed, owing, as he thought, to the stability of the nitro-compound and its easy volatility with water vapor. It was thought that these difficulties might be overcome by dissolving the compound in glacial acetic acid, treating with a solution of chromic anhydride in glacial acetic acid, and heating gently.

10 grams nitro-mesitylene were dissolved in 25 cc. concentrated acetic acid, and the solution of chromic anhydride gradually added, waiting each time until the pure green color indicating complete reduction appeared. The reaction did not take place at the ordinary temperature, so the solution was heated on the water-bath to 60° or 70°. When, on further addition of the solution of chromic anhydride, its color did not change to pure green, even after heating for several hours, the heating was stopped. The whole was then diluted with a considerable volume of water. A white precipitate settled. This was filtered, washed, and recrystallised from water and alcohol. The product was an acid not readily soluble in water. The melting-point was not sharp. It showed slight indications of melting at about 200°, very distinct at 219°–220°, and was completely melted at 225° (corrected). Recrystallisation did not change the melting-point. As the two isomeric nitro-mesitylenic acids are readily separated by means of their barium salts, the acid in hand was converted into the barium salt, and this subjected to crystallisation until only a very small quantity remained. The acid was then reprecipitated from a hot

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[1] Annalen der Chemie **147**, 8.
[2] *Ibid.* **150**, 325.
[3] *Ibid.* 193.
[4] *Ibid.* **179**, 165.
[5] *Ibid.* **147**, 3.

solution of the purest portion of the salt, and the melting-point was found to be essentially the same as before. The melting-point given by Jacobsen[1] for the para-acid, when precipitated under the above conditions, is 179°, and, when precipitated from absolute alcohol, 223° (corr.). Schmitz[2] had previously observed this peculiar conduct, though he gives the melting-points somewhat lower than Jacobsen, and, according to him, they are not sharp. His acid, when melting at the upper point, showed indications of melting as low as 200°. He says, however, that there could be no doubt regarding the purity. With the acid obtained in my experiments the lower melting-point was in no case obtained first, but it was noticed that, on allowing the specimen to cool in the capillary tube, it did not solidify until the temperature 164°–163° was reached, and there was no variation in this, except in a few cases in which it solidified not far below the melting-point, probably on account of imperfect melting. At all events, in these cases, on again melting and allowing to cool, it solidified at 164°–163° (corr.). If the specimen was now heated before it had cooled to 100°, or in some cases as low as 85°, depending apparently on the conditions of cooling, it melted at 174°–176° (corr.), the lower melting-point given by Schmitz.

The acid precipitated from the most soluble part of the barium salt melted exactly like that from the first portion of salt, and conducted itself in the same way, so that apparently only one product was formed.

The nitro-acid was converted into the amido-acid by treating it with tin and hydrochloric acid. The product melted at 245° (uncorr.), with partial decomposition. The melting-point given by Fittig for this acid is 235°. The amido-acid was converted into the oxy-acid according to the directions given by Jacobsen.[3] The resulting acid gave no color reaction with ferric chloride, was not volatile with water vapor, and melted at 218°–222°. From these facts it is clear that the nitro-acid is para-nitro-mesitylenic acid. Therefore, nitro-mesitylene conducts itself towards chromic acid in the same way that brom- and chlor-mesitylene do, the nitro-group protecting the two ortho-methyls.

Thinking that, in consequence of the presence of the strongly acid sulpho-group in free sulpho-mesitylenic acid, the oxidation with chromic acid might take place as with nitro-mesitylene, an attempt was made to oxidise some of the free acid with a solution of chromic anhydride in glacial acetic acid. The experiments gave negative results, the acid being burned up. An experiment with mesitylene-sulphamide and chromic anhydride in solution in glacial acetic acid was equally unsuccessful.

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[1] Berichte d. deutsch. chem. Gesell. **11**, 2054.

[2] Annalen der Chemie **193**, 160.

[3] Berichte d. deutsch. chem. Gesell. **12**, 608.

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ACTION OF CONCENTRATED SULPHURIC ACID ON HYDRAZINE-TOLUENE-SULPHONIC ACIDS.

By E. A. Schneider.

At the suggestion of Professor Remsen I have recently tried some experiments in the hope of obtaining a condensation between the hydrazine group and the sulpho-group in the hydrazine-sulphonic acids, a condensation which did not appear improbable in view of the fact that E. Fischer[1] obtained a hydrazine-benzoic anhydride. For this purpose I treated *p*-hydrazine-toluene-*m*-sulphonic acid, $C_6H_3\left\{\begin{array}{l}CH_3\\ SO_3H\ (m)\\ N_2H_3\ (p)\end{array}\right.$, and *p*-hydrazine-toluene-*o*-sulphonic acid, $C_6H_3\left\{\begin{array}{l}CH_3\\ SO_3H\ (o)\\ N_2H_3\ (p)\end{array}\right.$, with concentrated (66°) sulphuric acid. 10 grams of the latter acid were gradually added to the concentrated sulphuric acid. The evolution of heat was only very slight. In order to effect perfect solution of the hydrazine-sulphonic acid the mixture was heated to 170°. At this temperature the sulphuric acid became dark in color, and the odor of sulphurous acid was observed. After this temperature had been maintained for a few minutes the solution was poured into a large volume of cold water. The resulting yellow liquid remained perfectly clear, even after standing for some time. Caustic soda produced a distinct odor of ammonia, but there was no separation of a solid substance, even after long standing of the liquid.

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[1] Annalen der Chemie **212**, 333.

Under similar circumstances *p*-hydrazine-toluene-*m*-sulphonic acid conducted itself entirely differently. On bringing it into concentrated sulphuric acid there was no perceptible evolution of heat. To effect complete solution it was necessary to apply heat. It was observed that, as soon as the temperature of the sulphuric acid reached 80°, a violent reaction took place, accompanied by foaming and evolution of sulphurous acid. In this stage of the reaction the liquid was poured into a large volume of cold water. There separated at once a bright red, amorphous powder, which increased in quantity by standing. 90 grams of the hydrazine acid gave 10 grams of the red substance when treated as above described. It is soluble in concentrated acids with the aid of heat, and in dilute alkalies. From solutions in acids it is precipitated by water, from the solutions in alkalies by acids. I have not further investigated the product.

The brownish-yellow solution filtered from the red substance was now treated with alkali in excess. This caused the precipitation of a yellow, flocculent substance which in its whole conduct exhibited a striking resemblance to the basic substance which Gallinek and v. Richter[1] recently obtained by heating *p*-tolylhydrazine with sulphuric acid and afterwards neutralising the acid solution with caustic soda. I prepared this substance according to the directions given by Gallinek and v. Richter, in order to compare it with the substance obtained by me. The following points of resemblance were noted: Both substances are strong bases; they combine with concentrated acid with marked evolution of heat, forming easily soluble salts, the dilute solutions of which show the same yellow color; platinum chloride produces brownish-yellow, amorphous, insoluble precipitates in the hydrochloric acid solutions; both substances are practically insoluble in the ordinary solvents.

The yield from 90 grams hydrazine-toluene-sulphonic acid amounted to about 13 grams. The following nitrogen determinations, which were made with both bases, indicate that in all probability they are identical. The base from tolyl-hydrazine was found to contain no sulphur, while that from the hydrazine-sulphonic acid contained 2.57 sulphur. Further purification afterwards removed this. The differences in the percentages of nitrogen found in the two bases are probably to be ascribed to the presence of an impurity in the base obtained from the hydrazine-sulphonic acid.

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[1] Berichte d. deutsch. chem. Gesell. **18**, 3172.

Base from Para-tolyl-hydrazine.

	Found.	
	I.	II.
N	12.94	12.84

Base from Hydrazine-sulphonic Acid.

	Found.		
	I.	II.	III.
N	12.04	11.38	11.45

Platinum Double Salt of the Base from Para-tolyl-hydrazine.

	Found.	
	I.	II.
Pt	25.46	25.61

Platinum Double Salt of the Base from Hydrazine-sulphonic Acid.

	Found.	
	I.	II.
Pt	22.44	22.83

In order further to purify the base from hydrazine-sulphonic acid, it was suspended in absolute alcohol, and a sufficient quantity of hydrochloric acid added to form the hydrochloride. This was then filtered off and washed with alcohol and ether. A determination of platinum made in the base purified in this way gave 25.87 per cent. Pt. This figure agrees fairly well with that found in the case of Richter's base. In order to avoid conflicting with the work of Gallinek and von Richter I have not continued the investigation further.

It appears probable from the facts mentioned that, when *p*-tolylhydrazine is treated with concentrated sulphuric acid, it is first converted into *p*-hydrazine-toluene-sulphonic acid, and that this then, by further action of the concentrated sulphuric acid, is transformed into the basic substance.

A METHOD OF SEPARATING THE TWO ISOMERIC TOLUIDINE-SULPHONIC ACIDS.

By E. A. Schneider.

While working with the toluidine-sulphonic acids for the purpose of making the hydrazine-sulphonic acids used in the above experiments, I made the observation that the potassium salt of *p*-toluidine-*m*-sulphonic acid, which is very easily soluble in water, is insoluble in cold caustic potash, while the potassium salt of *p*-toluidine-*o*-sulphonic acid is extremely easily soluble in the same liquid at ordinary temperature. The same is true of the corresponding sodium salts. If it is desired to separate a mixture of the two acids into its components it is only necessary to heat it with concentrated caustic potash until it has all passed into solution. If this solution is allowed to cool slowly, the potassium salt of *p*-toluidine-*m*-sulphonic acid crystallises out in stout needles, which can be easily separated from the mother-liquor by means of a platinum cone and a filter pump. It is advisable to wash the salt in the funnel with alcohol and then quickly to press it between layers of filter paper.

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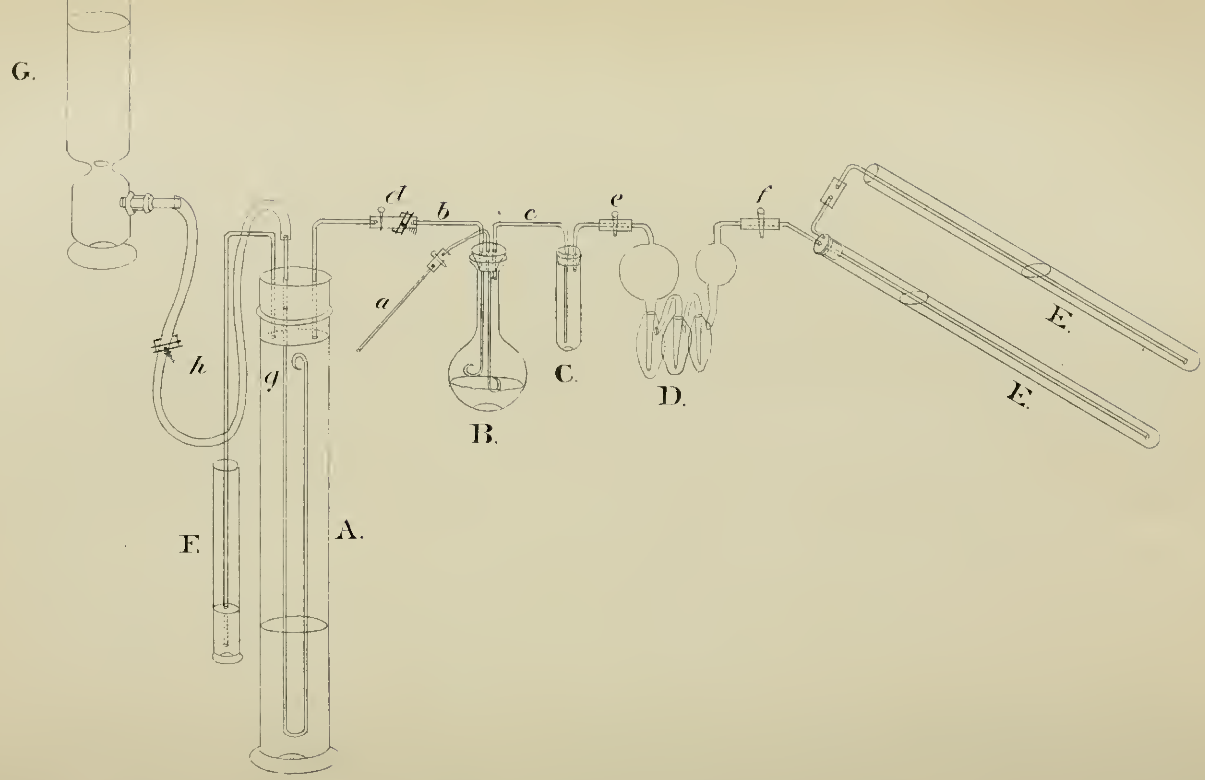
THE DETERMINATION OF NITRIC ACID BY THE ABSORPTION OF NITRIC OXIDE IN A STANDARD SOLUTION OF PERMANGANATE OF POTASSIUM.

By H. N. Morse and A. F. Linn.

The method which we propose consists in the conversion of the nitric acid into nitric oxide; the absorption of the latter in a measured but excessive quantity of a standard solution of permanganate of potassium; and the subsequent determination of the excess of the permanganate by means of a standard solution of oxalic acid, or sulphate of manganese.


G.
h
F.
g
A.
d
b
a
c
B.
C.
e
D.
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E.
E.

The Apparatus.

A is an apparatus for the generation of carbon dioxide free from air, which will be explained hereafter.

B is a flask, having a capacity of 125 or 150 cc., in which the nitrate is decomposed in the usual manner by means of ferrous chloride and hydrochloric acid.

C is a small tube for the condensation of the aqueous hydrochloric acid which distils over from *B*.

D is a Geissler bulb containing a concentrated solution of potassium carbonate, to arrest any acid vapors coming from *C*.

E, *E* are two pieces of ordinary combustion tubing, having a length of about 650 or 700 mm., in which is placed the permanganate solution employed for the absorption of the nitric oxide. Their open ends are provided with lips in order to facilitate the pouring of liquids from them, care being taken not to so distort the ends that rubber stoppers cannot be made to fit them tightly. They are placed in a nearly horizontal position in order to diminish the pressure required to force the gases through the apparatus and thus lessen the danger of leakage through the rubber joints.

a is a tube through which the ferrous chloride and hydrochloric acid are introduced into *B*, as in the method of Tiemann–Schulze.

b serves for the introduction of carbon dioxide to expel the air before the decomposition of the nitrate, and the nitric oxide afterwards.

c is an unbroken tube ending at the lower surface of the stopper in *B*, and at the bottom of *C*.

The rubber joint *d* is furnished with a Mohr and also a screw pinch-cock. The joints *e* and *f* are furnished with Mohr pinch-cocks. The rubber tubing upon these should be of the best quality and must be carefully tied.

The Solutions.

In consequence of the large volume of the permanganate solution required for the complete absorption of the nitric oxide, we have found it advantageous to use three solutions instead of two.

1. A solution of permanganate such that one cc. is equivalent to about fifteen milligrams of nitrate of potassium, according to the reaction: $KMnO_4 + NO = KNO_3 + MnO_2$.

This solution is employed for the absorption of the nitric oxide.

Its strength need not be exactly known. There is no objection to a more concentrated solution, except that which pertains to all strong standard solutions—namely, that a small error in measurement would then give a larger error in the results. 100 cc. of this solution are required for each determination, and the measurement is always made in one and the same 100 cc. measuring flask, which, if necessary, should be labelled to distinguish it from that used for solution No. 2.

2. A solution of oxalic acid which is very slightly stronger than that of the permanganate just described—that is, a solution such that one cc. of it will somewhat more than decompose one cc. of the permanganate, according to the reaction:

$$2KMnO_4 + 3H_2SO_4 + 5C_2H_2O_4.2H_2O = K_2SO_4 + 2MnSO_4 + 18H_2O + 10CO_2.$$

The exact strength of this solution need not be known, since we only require the difference in value between it and solution No. 1, which is determined by means of solution No. 3. 100 cc. of this solution are also required for each determination, and the measurement, as in the preceding case, is always made in the same 100 cc. measuring flask.

3. A dilute, carefully standardised solution of permanganate of potassium.

The method of using these solutions is as follows: 100 cc. of No. 1 and No. 2 are measured off (each solution in its own measuring flask), brought together in a covered beaker glass, and acidified with dilute sulphuric acid. The excess of oxalic acid is then determined by means of solution No. 3.

When it is desired to make a determination of nitric acid, 100 cc. of solution No. 1 are measured off, and as much of it as may be convenient is poured into the tubes *E*, *E*, together with about a gram of zinc sulphate for each tube, which substance appears to considerably facilitate the absorption of the nitric oxide by the permanganate. When the operation is over the contents of *E*, *E* are poured into a beaker glass. 100 cc. of solution No. 2 are then measured off, and a portion, together with a little sulphuric acid, poured into *E*, *E* to dissolve the oxide of manganese which has separated during the absorption of the nitric oxide. The oxide having been dissolved, the liquid in *E*, *E*, and the rinsings of the tubes, also the residues of permanganate and oxalic acid left in the measuring flasks, and the rinsings from these, are all brought together in the same beaker glass. Finally, the amount of solution No. 3 required to decompose the excess of oxalic acid is determined. If we subtract from the amount thus found the quantity of permanganate required to equalise solutions Nos. 1 and 2 (previously ascertained), we shall have the amount of permanganate actually reduced by the nitric oxide, according to the reaction:

$$6KMnO_4 + 10NO = 3K_2O + 6MnO + 5N_2O_5;$$

in other words, on the basis that one molecule of potassium permanganate will oxidise one and two-thirds molecules of nitric oxide

$$(KMnO_4 = 1\tfrac{2}{3}NO).$$

The method of using the apparatus is simple. The nitrate is placed in *B* and the joints made tight, except that at *f*, which is left open. A current of carbon dioxide is passed through the apparatus until all of the air has been displaced. Connection is then made at *f*, and soon afterwards the current of carbon dioxide is shut off at *d*.

The flask *B* is now heated as long as may be necessary in order to produce, on cooling, the diminished pressure required for the introduction of the ferrous chloride and hydrochloric acid. Before removing the flame the joint at *f* is closed to prevent the return of the permanganate solution.

As soon as the flask *B* has become sufficiently cool the ferrous chloride and hydrochloric acid are introduced through the tube *a* (which has been full of water from the first) in the same manner and quantities as in the well-known Tiemann-Schulze method.

The pinch-cock at *d* is then opened, and the apparatus allowed to fill with carbon dioxide. When the pressure has become sufficient to force the gas through the solution of permanganate the pinch-cock at *f* is removed. It should be opened only slightly and with great caution at first, unless one is certain that the pressure is sufficient. If the pressure is insufficient the fact will be made apparent by a rise of the permanganate in the small internal tube.

The flow of carbon dioxide is now reduced to a very slow current, or entirely cut off. The contents of *B* are slowly heated until the decomposition of the nitrate is complete and the greater part of the nitric oxide has been expelled, when the apparatus is again closed at *f* and *d* and allowed to cool. The tube *a* is then washed out by the introduction through it into *B* of a few cubic centimeters of strong hydrochloric acid.

The process of filling the apparatus with carbon dioxide, and of heating the contents of *B*, is repeated. When it becomes apparent, from the light color of the liquid in *B*, that all of the nitric oxide has been expelled from it, the current of carbon dioxide is increased and the heating discontinued. Care must be taken, however, not to admit too strong a current of carbon dioxide, lest some of the nitric oxide should be forced unabsorbed through the permanganate solution. It is also necessary, for the same reason, to avoid too rapid heating during the decomposition of the nitrate.

When all of the nitric oxide has been forced into the solution of permanganate the determination is made in the manner already described.

To test the method, nine determinations were made with quantities of pure nitrate of potassium varying from 100 to 200 milligrams. The maximum difference between the volumes of permanganate actually used and those calculated was 0.05 cc., while the main difference was 0.036 cc. The measurements of the permanganate were made from a burette which had been carefully calibrated. We also made a number of determinations, using a solution of manganous sulphate in the place of the oxalic acid. The advantage of this method lies in the fact that it is not necessary to dissolve the oxide which is precipitated upon the glass within the tubes *E*, *E*, since, in the presence of an excess of permanganate, the reduction by nitric oxide extends only to the formation of MnO_2; also in the fact that the solution of manganous sulphate is more stable than that of oxalic acid. A solution of the sulphate having been once carefully standardised, can be used for a long time to determine the value of permanganate solutions.

The details of the method are as follows: A solution of manganous sulphate slightly stronger than No. 1 is prepared.

The difference between 100 cc. of it and 100 cc. of No. 1 is ascertained, according to the method of Volhard, by means of solution No. 3.

The contents of *E*, *E*, together with the rinsings from the tubes, are poured into a capacious flask. 100 cc. of the manganous sulphate and a few drops of nitric acid are then added and the whole boiled. Finally, the excess of manganous sulphate is determined, in the manner described by Volhard, by means of solution No. 3. Subtracting from the total amount of permanganate thus used the quantity required to equalise the 100 cc. of solution No. 1 and the 100 cc. of the manganous sulphate, we shall have the quantity of permanganate reduced by the nitric oxide.

It must, however, be remembered that the value of solution No. 3 is now to be calculated on the basis of the equation $KMnO_2 + NO = KNO_3 + MnO_2$. One molecule of permanganate equals one molecule of nitric oxide when manganous sulphate is used, since no part of the permanganate employed in this method is reduced below the superoxide condition. In other words, solution No. 3 now represents only three-fifths as much nitric acid as it does when oxalic acid is used.

The results obtained by this method were moderately satisfactory, but not quite so exact as those obtained when oxalic acid was used. A series of four determinations gave differences, between the volumes of permanganate calculated and used, of 0.05 to 0.15 cc.

The principal objection to the method lies in the difficulty of determining, in the presence of the brown oxide of manganese, the exact point at which the oxidation is complete.

The carbon dioxide generator *A* was devised by us to take the place of the ordinary generators, in which marble is used. We have found that a submersion of twenty hours in boiling water does not suffice to completely remove the air which, as is well known, is contained in ordinary marble; hence some other substance must be employed as a source of the gas. In the apparatus which we are about to describe the acid carbonate of sodium is used.

It consists of a long narrow cylinder (450 × 60 mm.); a tightly-fitting rubber stopper, through which three tubes pass, as shown in the figure; a small cylinder *F*, containing mercury; and a sulphuric acid reservoir *G*.

The tube *g* is drawn out to a fine point at the end and curved, so that the acid which is delivered into *A* falls upon and runs down the outside of the tube. The tube *h* dips under the mercury in *F*. *G* and *g* are connected by means of a long piece of rubber tubing which is supplied with a screw pinch-cock.

The apparatus is made to give any required pressure by raising or lowering *G* and *F*; but the elevation of *G*, as compared with that of *F*, should always be such that the gas will force its way through *h* rather than *g*. The upper part of the cylinder *F* is filled with cotton wool to prevent loss of mercury by spattering.

The material placed in *A* consists of a saturated solution of acid carbonate of sodium to which an excess of the solid salt has been added. The sulphuric acid is the ordinary dilute. The apparatus, if properly regulated, serves its purpose very well. The principal precaution to be observed in using it is to avoid a too sudden relieving of the pressure, which would, of course, result in the introduction of an unnecessarily large quantity of sulphuric acid into *A*.

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INVESTIGATION ON THE ATOMIC WEIGHT OF TUNGSTEN.

BY JOHN WADDELL, Ph. D. (Heidelberg), D. Sc. (Edin.).

Owing to theoretical considerations which need not be here detailed, I was led to doubt the accuracy of the atomic weight of tungsten which has usually been accepted as correct, and an investigation of the literature of the subject did not satisfy me that sufficient care had been taken to ensure the purity of the materials employed. Molybdenum and silica especially are impurities likely to occur, and little evidence was afforded that they were absent in the compounds from which the atomic weight of tungsten was estimated.

The method of purifying by recrystallisation, though the one almost universally adopted, seemed open to objection, and I decided to try the method of fractional precipitation. In order to carry out this process it was necessary to prepare an alkaline tungstate, and it was advisable to have it as pure as possible before proceeding with the precipitation. It was designed to get a series of precipitates of such a character that, if pure from admixture, tungstic acid could be readily obtained, by the reduction of which to metallic tungsten the data necessary for atomic-weight determination are afforded. Similarity of composition in the precipitates was to be taken as a guarantee of purity; for it was unlikely that impurities present would be thrown down in the same proportion in all the fractionations. If a difference occurred in the precipitates, those at the extremes should be most unlike, while those near the middle should have practically the same composition, and might fairly be accepted as pure. This paper is to be devoted chiefly to a description of how the above plan was carried out, with an account of some of the difficulties encountered and the precautions adopted, together with the results arrived at by the investigation.

Some preliminary experiments were made with scheelite, in order to test methods of separation of silicon and molybdenum, both of which were present in the mineral. Scheelite is essentially calcium tungstate; the sample I worked with also contained iron in some form. The mineral was disintegrated by boiling with aqua regia, and the soluble chlorides filtered off from the portion insoluble in acid. This precipitate was bright yellow in color, and along with tungstic acid contained considerable silica and a little molybdic acid. Attention was first directed to methods of separating silica, two methods being tried. The first was fusion of the mixture of silica and tungstic acid with potassium hydrogen sulphate, by which operation soluble tungstate (with molybdate when molybdic acid is present) is produced, the silica being unattacked. Details of the operation are given in the appendix. The solution of tungstate and sulphate having been obtained free from silica, the next step was to precipitate the tungsten in some form.

Theoretically it is possible to precipitate tungstic acid from a mixture of alkaline tungstate and sulphate by heating with sulphuric acid. In this process care must be taken to regulate the temperature properly, for if too low the tungstic acid does not separate out, and if too high the mass fuses and reproduces the original tungstate. This method, which may be used with small quantities, though even in such cases probably not very satisfactory, did not seem capable of application on the large scale. A method of separation common enough in quantitative analysis is to use mercurous nitrate as a precipitant. Mercurous tungstate is thrown down, and from that precipitate tungstic acid can be obtained either by sublimation of the mercury or by extraction of the latter with aqua regia. I thought that this method might prove of use for fractional precipitation, and proceeded to test it. I found that the mercurous tungstate is difficult to filter, the precipitate having a tendency to run through the paper. The same difficulty presents itself in filtering the tungstic acid obtained by treatment of the mercurous tungstate with aqua regia. These obstacles were not insurmountable, however, for if water containing mercurous nitrate be used for washing the tungstate the filtration can be carried on successfully. In the same way very dilute hydrochloric acid, if used to wash the precipitate of tungstic acid, makes the operation of filtering quite easy.

A much more serious difficulty was presented by the sparing solubility of mercurous salts. It was only possible to make a dilute solution of mercurous nitrate, and even this dilute solution seemed to precipitate sulphate as well as tungstate. I found that mercurous nitrate continued to give a precipitate, though excess of mercury seemed to be present, a test portion of the liquid giving with hydrochloric acid a precipitate of mercurous chloride, as also a precipitate with sulphuretted hydrogen. The use of large quantities of liquid being disadvantageous, this method of separation was abandoned. The second method of separation of silica and tungstic acid tried was digestion with ammonia. The best method for carrying out the operation is described in the appendix. As a result of my work some ammonium tungstate was obtained, but the extraction of the tungstic acid was not complete. Later experience indicated slight improvements in detail, such as would make the extraction more perfect, but in the meantime a material had been obtained almost free from silica.

Of the preliminary work it only remains to describe the process employed for eliminating the molybdenum. Some of the ammonium tungstate above described, which contained part at least of the molybdenum originally in the scheelite, was changed into the sodium salt by fusion with sodium carbonate. To a solution of tungstate thus obtained enough tartaric acid was added to prevent precipitation of tungstic acid by acidification with hydrochloric acid. A stream of sulphuretted hydrogen, passed for several hours, formed a slight precipitate, which gave the borax and microcosmic beads characteristic of molybdenum. The filtrate was evaporated to dryness in a platinum basin and the mass heated till it began to char. Potassium nitrate was added in small portions till the carbon was all oxidised and a white mass obtained, mainly tungstate, but containing chloride and carbonate as well. These impurities presented no special disadvantages, but the process of evaporation of the tartrate and subsequent ignition with nitre was troublesome.

The process of elimination of silicon and molybdenum seemed, therefore, likely to prove no easy task. I hoped to avoid the difficulty by using as starting-point a material containing neither of these impurities. With this view I procured commercial tungsten, a dark gray powder containing 94–98 per cent. of the metal. I was assured by the manufacturer that molybdenum was absent. At the outset I was met by the difficulty of getting the material into a workable form. So slowly is it attacked by acids, that my attempts to oxidise it by aqua regia were very imperfectly successful. Better results were obtained by throwing a mixture of the metal with nitre into a red-hot crucible. The crucible itself was attacked, however, and a third method was tested. On the small scale the results were good, and considerable attention was devoted to the determination of the most favorable conditions. The method consisted in igniting a mixture of potassium chlorate, sugar and metal. Evidently what was desired was a high temperature and a large quantity of available oxygen. The proportions found most suitable were—chlorate nine parts, sugar three parts, tungsten five parts. The oxidation was in this way very rapid, but from the potassium tungstate thus produced it was almost impossible to get a fair yield of tungstic acid, owing to the presence of the large quantity of other salts. A much more satisfactory mode of oxidation was by the direct action of air at a high temperature. The commercial tungsten was placed in a porcelain tube in a Fletcher's furnace and heated to redness in a current of air. Fumes of sulphurous acid were evolved, and were absorbed by a caustic soda solution. In this solution molybdic acid was afterwards found, though only in very small quantity. At the end of six hours the tungsten was oxidised to a greenish mass. The color was due to imperfect oxidation. When the roasting was continued for about thirty hours a yellow powder was obtained, there being very little, if any, unoxidised tungsten. The green substance, however, was quite suitable for further manipulation, as it contained only about 5 per cent. of unoxidised material, and this was readily separated.

A preliminary experiment showed that it would be impossible to extract the tungstic acid from the green powder by boiling with solution of caustic soda. I therefore fused it with half its weight of carbonate of soda, digested the fused mass with water, and filtered off from the unoxidised residue. The filtrate was evaporated in a large silver basin with addition of ammonium carbonate, the precipitate formed filtered off, and the filtrate evaporated down as before, the process being repeated till the carbonate produced no more precipitate. The total precipitate was very small, and proved to be chiefly, if not entirely, alumina. During the evaporation a thin, copper-colored film appeared on the silver basin. This film was soluble in hydrochloric acid, giving a blue solution, which became decolorised on exposure to the air or addition of a drop of nitric acid. The film was evidently some compound of tungsten, and I believe that titanium salts give similar deposits in platinum vessels.

The clear solution of tungstate, which naturally contained carbonate, was evaporated to small bulk, and thus crystals were obtained. As, however, the mother-liquor was quite colorless and clear, I continued the evaporation to dryness. In this way I prepared nearly three kilos of mixed tungstate and carbonate. In a trial portion of this substance I proved the presence of an appreciable, though small, quantity of molybdenum.

After considerable investigation I was not able to find a more convenient method for separating molybdenum and tungsten than the one already given, which is recommended by Rose. I found, however, that the subsequent elimination of tartaric acid was unnecessary for my purpose. I discovered that, while the presence of no very large quantity of this acid prevents the precipitation of tungstic acid by *cautious* addition of a *little* hydrochloric acid, a considerable excess of the latter, even if slowly added, gives a precipitate. This precipitate can be redissolved by tartaric acid in *large* excess *only*, but, once redissolved, *much* hydrochloric acid can be added before precipitation again occurs.

A solution of 300 grams of tungstate was added to a solution of 150 grams of tartaric acid, and the molybdenum separated as above described. The filtrate had a blue color, evidently due to some reduction of the tungstate; but a current of air passed for several hours through the solution decolorised the liquid, which was then ready for fractional precipitation.

The fractionations were made in the following manner: To the boiling solution in a porcelain basin 20–30 cc. hydrochloric acid, 1.135 sp. gr., were added and the boiling continued till considerable precipitate appeared. The contents of the basin were then removed to a large beaker (about two litres) and hot water added (if necessary) to fill the beaker. When the tungstic acid had settled the clear supernatant liquid was decanted and the precipitate washed twice by decantation. Further washing was impossible, unless with addition of hydrochloric acid, for the tungstic acid did not settle, but made the liquid milky. Sometimes the acid necessary for the subsequent precipitation was added to the last washing. The decantations were evaporated to the bulk of the original solution, and if the requisite acid had not before been added it was now poured in and another precipitation obtained.

In this way eleven fractionations were prepared of these; the first was dark green, those following as far as the seventh were light yellow, while the remaining ones were dirty green and not so finely divided as the preceding. The color of the first precipitate was probably due to want of complete oxidation by the current of air passed through the liquid, while the condition of the final fractionations was doubtless caused by the fact that, in order to get a reasonable quantity of the tungstic acid, evaporation to small bulk was required. The tartaric acid probably under these circumstances exercised a reducing action, while the continued boiling promoted coagulation.

For the atomic-weight determinations three of these fractionations were purified—viz.: III, X and VII. A description of the treatment of III will show the general method. The precipitate was washed several times by decantation, and then repeatedly on a filter with very dilute (say 3 per cent.) hydrochloric acid. It was afterwards dissolved in ammonia, filtered from the very trifling residue and reprecipitated by hydrochloric acid (the best method is by pouring the boiling solution into excess of hydrochloric acid). This precipitate was again washed by decantation and on the filter till the washings yielded no residue on evaporation, and a test portion of the precipitate gave only a slight indication of sodium by the spectroscope.

The hydrochloric acid used was freed from a possible trace of arsenic by digestion with copper foil, and was afterwards three times distilled. The ammonia was redistilled from baryta. Both it and the acid were proved to be free of anything leaving a solid residue on evaporation. The precipitate was dried, powdered, and heated to redness in a current of air, in order to get rid of the last traces of hydrochloric acid and ammonium chloride, and to ensure complete oxidation. This ignition lasted several hours. The tungstic acid thus obtained was quite uniform in appearance, and of a beautiful pale canary-yellow color.

Some of this tungstic acid was afterwards reduced in a current of hydrogen (purified by passing through large U-tubes containing pumice moistened respectively with lead nitrate, silver nitrate, caustic potash and strong sulphuric acid). Care was taken to increase the temperature gradually, in order to prevent the tungstic acid from volatilising before reduction. The temperature was finally raised to the highest attainable by a strong blast in Fletcher's furnace. The material before and after reduction was weighed in a porcelain boat enclosed in a glass weighing-tube, and counter-balanced by a similar tube containing an empty boat. In order to see whether volatilisation had taken place, the porcelain tube in which the substance had been heated was wiped out with cotton wool, and when the wool remained perfectly clean it was assumed that there had been no volatilisation. Several experiments showed that very slight amounts of volatilisation were capable of being thus detected. At the highest temperature of the furnace there was danger of the boat fusing to the tube unless protected in some way. The plan adopted was to wind a couple of pieces of platinum wire about the boat. Contact with the tube was thus prevented.

I assumed, as has always been done, that hydrogen reduces tungstic acid to metallic tungsten. I proved that no hydrogen is occluded by weighing one specimen of the metal obtained as above, and afterwards heating it to redness under diminished pressure and again weighing. The weight was constant. The fraction X, to which XI was added, was subjected to the same treatment as III, but never attained the same stage of apparent purity. During the reduction, too, a slight volatilisation occurred. I therefore purified VII with quite satisfactory results, and the atomic-weight determination was only slightly below those obtained with III. Subjoined is a table of determinations;

Fraction.	WO_3 taken.	W left.	O_3 lost.	Atomic wt.	Remarks.
III.	[1]1.4006	1.1115	.2891	184.55	No volatilisation.
	.9900	.7855	.2045	184.37	
	1.1479	.9110	.2369	184.59	
VII.	.9894	.7847	.2047	184.00	
X.	4.5639	3.6201	.9438	183.67	Slight volatilisation.

[1] Weights are in grams.

The mean of the atomic weights as determined in III is 184.5, if oxygen be regarded as 16. If O = 15.96, then W = 184.04. The estimation in VII so nearly agreed with the others that it was not thought necessary to make any further determinations.

I think there can be no doubt that the commonly accepted atomic weight is practically correct. It is useless to attempt to be more accurate while the atomic weights of such elements as oxygen are open to dispute.

I made some determinations of atomic weights in precipitates from tungstate which had not been freed from molybdenum. The first fractionation was most carefully examined. It might naturally be expected to contain the greater portion of the molybdic acid, in which case a low result was to be looked for, not only because the atomic weight of molybdenum is only about half that of tungsten, but also because the experimental error of volatilisation is more difficult to avoid. A very slight volatilisation was observed, and as a mean of four experiments the number 183.68 was obtained. These determinations may be considered confirmatory of the more accurate ones, for the variation was just in the direction to be expected. Of course, by themselves they are of little value.

The precipitates obtained by fractionation gave practically concordant results, and hence pointed to absence of impurity. I, however, tested independently for silica by fusing with sulphate. A test experiment proved that the sodium salt acted in the same way as the potassium salt. To the mixed sodium tungstate and carbonate which had been used for my investigations I added a few drops of strong sulphuric acid and fused as described in the appendix. No silica was found.

I made two determinations of specific gravity, one of metal not specially freed from molybdenum, another of a portion of III which was considered pure. The numbers obtained were 18.25 and 18.77. These so nearly corresponded with the determinations of other investigators that I did not pursue the matter further. The second determination is doubtless the more accurate.

The result of my work has therefore been confirmatory of the accuracy of previous investigations. So far as I am aware, the method of operation has not been applied to tungsten before, and the agreement affords a trustworthy corroboration.

APPENDIX.

The separation of silica and tungstic acid by fusion with potassium hydrogen sulphate is troublesome unless attention be paid to some important details. About equal weights of the sulphate and mixture of tungstic acid and silica are fused till the evolution of sulphuric anhydride almost ceases. The fused mass should then be limpid and flow quietly. This is the stage when the acid sulphate $KHSO_4$ is changed to the compound $K_2S_2O_7$. The silica should be seen floating about in the fused mass. The crucible having been cooled, the fused mass should be powdered and added to boiling water. After further boiling the undissolved material should be allowed to settle and the supernatant liquid decanted through a filter. Fresh water is added to the residue and again boiled and decanted. Further washing with pure water will probably be found impracticable, because the precipitate tends to run through the filter. Dilute ammonium carbonate should then be employed. This dissolves the remaining tungstate, as well as tungstic acid, the silica being left unattacked. After the precipitate is removed to the filter it should be washed a number of times with hot water containing ammonium carbonate.

As the last traces of tungsten are difficult to wash out, it is probably necessary for exact quantitative separation to dry the precipitate and fuse again with a little acid sulphate. In quantitative estimation also it will not be easy to powder the fused mass without loss. It is therefore best, under such circumstances, to remove the mass in lumps and digest with water for a longer time. The operation is slower, but otherwise equally good.

To dissolve tungstic acid in ammonia it is best to have the substance in a bottle. Then add a moderately strong but not saturated solution of ammonia, shake violently for several minutes, allow to settle, and decant the most of the supernatant liquid, add water to the remainder and shake again. Decant as before, and repeat the process if necessary. It may then be necessary to add a little more ammonia, but in most cases the tungstic acid will be entirely dissolved. It is of little, if any, advantage to use hot water.

FURTHER RESEARCHES ON COMPLEX INORGANIC ACIDS.[1]

By Dr. Wolcott Gibbs.

You will doubtless remember the very interesting and curious results obtained many years since by Schützenberger by the action of phosphoric pentachloride upon spongy platinum. We have simply $Pt + PCl_5 = PtCl_2.PCl_3$, the compound by the action of water giving the corresponding acid $PtCl_2.P(OH)_3$. A second and analogous compound chloride has the formula $PtCl_2.2PCl_3$, and this yields the acid $P_2.PtCl_2.(OH)_6$. A third acid has the formula $P_2.PtCl_2.(OH)_5$, and a fourth is represented by $P_2O_2.PtCl.(OH)_3$. These compounds have attracted very little attention, perhaps on account of the neglect and contempt into which inorganic chemistry has fallen of late years. Schützenberger does not appear to have attempted to generalise his results. I have endeavored to show, in a paper read before the National Academy of Science, that in Schützenberger's acids platinous chloride simply replaces an atom of oxygen, and that, by appropriate methods, we ought to be able to perform the inverse substitution and obtain three new acids of phosphorus which would have respectively the formulas $P_2O(OH)_6$, $P_2O(OH)_5$ or perhaps $P_4O_2(OH)_{12}$, and $P_4O_7(OH)_6$, since $2PtCl''' = 3O$. Of course the first acid mentioned above, $P.PtCl_2.(OH)_3$, is, on this view, orthophosphoric acid, in which $PtCl_2$ replaces one atom of oxygen. I have now succeeded in generalising these results in what seems to me an interesting manner. In the first place I have discovered compound acids analogous to chlorplatinorthophosphoric acid which contain respectively palladium, iridium, ruthenium and osmium in place of platinum. Want of material has prevented me from experimenting with rhodium also, but it can hardly be doubted that it forms similar compounds. In the next place I find that platinous chloride may be replaced by platinous oxide or bromide, and the same appears to be true for other metals of the platinum group. A still further generalisation consists in replacing phosphorus by arsenic and antimony, which is easily effected. It is to be expected that vanadium will yield similar compounds, but here again want of material has prevented the actual experiment up to the present time. The following formulas, which are, I believe, to be depended on, will serve to illustrate my results:

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[1] From a letter to the Editor.

$$As_2O_3.3[As_2O_3.2PtO]5(NH_4)_2O + 7Aq,$$
$$[As_2O_3.2PtCl_2]K_2O.2H_2O.$$

As I have written it, the first compound might be called an arsenoso-oxyplatin-arsenate, and the second a chlorplatin-arsenate. When these compounds are digested or boiled with acid tungstates and molybdates, higher complex acids are obtained which I am now studying. One tungsten compound appears to have the formula:

$$24WO_3.As_2O_3.3[As_2O_3.2PtCl_2]12Pt(NH_3)_4O + 60Aq.$$

Another, the formula:

$$22WO_3.3As_2O_3.3[As_2O_3.2PtO]6Pt(NH_3)_4O + 40Aq.$$

A beautiful pale green molybdenum compound has the formula:

$$12MoO_3.As_2O_3[As_2O_3.2PtO]2Pt(NH_3)_4O + 27Aq.$$

All these compounds contain the oxide of platino-ditetramine, $Pt(NH_3)_4O$, as a base. The formulas given, however, are only preliminary, and may hereafter prove reducible to simpler expressions. The salts were obtained by digesting or boiling the green salt of Magnus, $Pt(NH_3)_4Cl_2 + PtCl_2$, with arsenoso-tungstates and arsenoso-molybdates. Analogous series appear to be formed when arsenoso-phospho-tungstates and arsenoso-phospho-molybdates are digested or boiled with platinous chloride or with the tetramine salt. Now, replace platinum by other metals of the same group, and arsenic by antimony or phosphorus, perhaps also by vanadium, and you will have some idea of the extent of the new field of work in which I am now laboring as fast as my limited means and resources will permit.

NEWPORT, R. I., *July 1st.*

REVIEWS AND REPORTS.

THE ELEMENTS OF PHYSIOLOGICAL AND PATHOLOGICAL CHEMISTRY. By T. CRANSTOUN CHARLES, M. D. Philadelphia: Henry C. Lea's Son & Co. 1884.

The aim of the author to write "a hand-book for medical students and practitioners" appears to be very well carried out in this work, especially when one considers the difficulty of trying to teach what is in many respects advanced organic chemistry to persons who usually have, at best, only a general knowledge of the science. The book should be used in connection with a laboratory course, and it is well suited for this by the introduction of explicit directions for the separation and study of substances occurring in the animal body. As it is evidently made up from a pretty thorough review of the literature of the subject, it will also be of use as a work of reference to physicians who know sufficient chemistry to read any book of the kind intelligently.

A few very noticeable errors have been introduced into the book, such as the directions for preparing diastase from yeast. The chapter on respiration is quite brief, and the important subject of the changes that take place in the blood as a result of respiration does not receive the attention it deserves.

The use of structural formulas is not carried to the extent that one frequently finds in books on physiological chemistry, but it is doubtful if they should be used at all in a text-book of this class, and certainly they should not be applied to such compounds as $C_{44}H_{90}NPO_9$.

Although the book shows no great originality, its general plan is a good one, and there is reason to hope that it will be a means of increasing the slight knowledge of physiological chemistry usually found among physicians. J. R. D.

NOTES.

On the Constitution of Levulose and Dextrose.

Kiliani, in Munich, has undertaken to clear up the constitution of levulose and dextrose,[1] and, it must be added, very successfully. According to Kiliani, levulose is a ketone alcohol, dextrose either an aldehyde or an inner anhydride. He is at present endeavoring to answer this last question. Hydrocyanic acid has the power of forming addition-products with ketones. On this reaction Kiliani's investigation is based. If levulose is a ketone, its constitution can be expressed by either of the two formulas:

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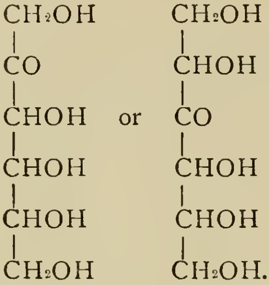
[1] Berichte d. deutsch. chem. Gesell. 1885, 3066; 1886, 767, 1128.

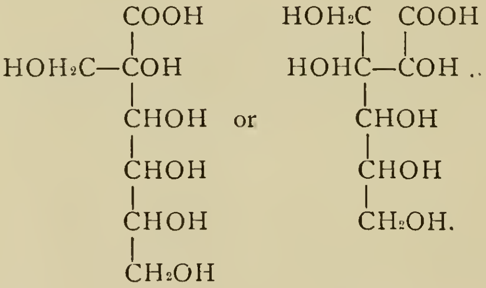
I. II.



$$\begin{array}{lcl} \text{CH}_2\text{OH} & & \text{CH}_2\text{OH} \\ | & & | \\ \text{CO} & & \text{CHOH} \\ | & & | \\ \text{CHOH} & \text{or} & \text{CO} \\ | & & | \\ \text{CHOH} & & \text{CHOH} \\ | & & | \\ \text{CHOH} & & \text{CHOH} \\ | & & | \\ \text{CH}_2\text{OH} & & \text{CH}_2\text{OH}. \end{array}$$

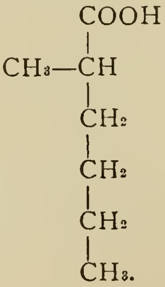
The carboxyl acids derived from the hydrocyanic acid addition-products of these two ketone alcohols must therefore have the constitution:

I. II.



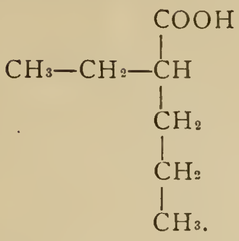
$$\begin{array}{rlcrl} & \text{COOH} & & \text{HOH}_2\text{C} & \text{COOH} \\ & | & & | & | \\ \text{HOH}_2\text{C}- & \text{COH} & & \text{HOHC}- & \text{COH} \\ & | & & | & \\ & \text{CHOH} & \text{or} & \text{CHOH} & \\ & | & & | & \\ & \text{CHOH} & & \text{CHOH} & \\ & | & & | & \\ & \text{CHOH} & & \text{CH}_2\text{OH}. & \\ & | & & & \\ & \text{CH}_2\text{OH} & & & \end{array}$$

I treated with concentrated hydriodic acid ought to yield methyl-normal-butyl-acetic acid:



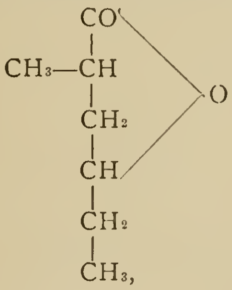
$$\begin{array}{rl} & \text{COOH} \\ & | \\ \text{CH}_3- & \text{CH} \\ & | \\ & \text{CH}_2 \\ & | \\ & \text{CH}_2 \\ & | \\ & \text{CH}_2 \\ & | \\ & \text{CH}_3. \end{array}$$

II treated in the same way ought to yield ethyl-propyl-acetic acid:



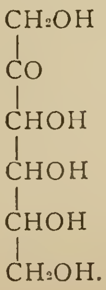
$$\begin{array}{l}COOH\\ |\\ CH_3—CH_2—CH\\ |\\ CH_2\\ |\\ CH_2\\ |\\ CH_3.\end{array}$$

Treating levulose with hydrocyanic acid, Kiliani obtained a crystalline addition-product—levulose-cyanhydrin—which on saponification with acids gave a carboxyl acid. It was not possible to obtain this acid in a pure condition. The raw product therefore was treated with hydriodic acid and red phosphorus, and a lactone, α-methyl-capro-lactone, as it was later proved to be,



was obtained. This lactone, treated again with hydriodic acid, yielded a heptylic acid. In order to decide if the acid thus obtained was a methyl-butyl-acetic acid or an ethyl-propyl-acetic acid, Kiliani prepared these compounds by means of the aceto-acetic ether synthesis.

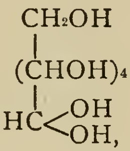
The properties of the synthetical methyl-normal-butyl-acetic acid coincided with those of the acid obtained from levulose. The constitution of levulose is, therefore, to be expressed by Formula I:



$$\begin{array}{l}CH_2OH\\ |\\ CO\\ |\\ CHOH\\ |\\ CHOH\\ |\\ CHOH\\ |\\ CH_2OH.\end{array}$$

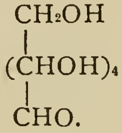
Kiliani treated dextrose in the same manner with hydrocyanic acid. He obtained a hexa-oxy-heptylic acid, which he calls dextrose-carboxyl acid. This acid, when treated with hydriodic acid and red phosphorus, yields normal heptylic acid. This fact proves that dextrose is not a ketone alcohol, or it could not yield a compound with a normal carbon chain.

There remains still to be answered the important question: Is dextrose an aldehyde or an anhydride? If we consider dextrose a derivative of the alcohol,



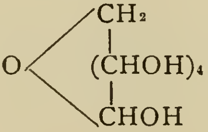
$$\begin{array}{c} CH_2OH \\ | \\ (CHOH)_4 \\ | \\ HC\begin{matrix} OH \\ OH, \end{matrix} \end{array}$$

we could formulate the same question thus: Are both hydroxyls which are subjected to dehydration combined with one carbon atom or with two? If either of these questions should be answered in the affirmative, we would obtain in the first case Baeyer's and Fittig's aldehyde formula:

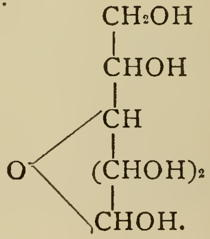


$$\begin{array}{c} CH_2OH \\ | \\ (CHOH)_4 \\ | \\ CHO. \end{array}$$

In the second case we would obtain one of the five possible anhydride formulas of Tollens; for instance:



or



At present the second possibility appears the more probable. V. Meyer showed—several years ago—that dextrose does not give the reaction with fuchsine-sulphurous acid—a reaction which is peculiar to aldehydes.

E. A. S.

VOL. VIII. [OCTOBER, 1886.] No. 5.

AMERICAN CHEMICAL JOURNAL.

OPIUM ANALYSIS.

BY CHARLES M. STILLWELL.

In presenting a method for the analysis of opium, as an addition to the many processes published from time to time, I feel justified on account of the importance which a correct analysis of this costly substance demands. I lay claim to no special originality in the general method of the analysis to be described. Based as it is upon the processes used by Dr. Squibb for the sampling of the opium and the mode of extraction and precipitation of the morphia, I have attempted to render these still more effective by such modifications as I find necessary in the course of the analysis. The use of the two washing solutions, to be described hereafter, is an important step toward obtaining a pure precipitate of morphia; and the final purification of the crystalline precipitate, proposed by myself, I find to be absolutely necessary for the correctness of the analysis. To this latter point I call special attention. The process of Dr. Squibb, used as he directs, will give results which are almost exactly comparable among themselves. It can be used, therefore, as a control; but to obtain analytical results such as are needed for buying and selling, a still greater degree of accuracy is required. For this purpose I believe the method now to be described to be of great value. It is presented somewhat more in detail than may seem necessary, but I find in my practice that much of the value of an analytical process depends upon these small and seemingly insignificant points. For the analysis of a substance so complex in its nature as opium, it is necessary that the process used should be simple, easy of manipulation, but yet thoroughly successful in the extraction of all the morphia present. The solvent used and the bulk of the solution obtained should be such that the least possible amount of injury is done to the alkaloid during the course of the analysis.

In Allen's *Commercial Organic Analysis* is found the following account of the

Action of Solvents on Opium.—"The action of different solvents and reagents on opium is shortly as follows:

"Water dissolves meconic acid readily, as also meconate and acetate of morphia; free morphia very sparingly, and narcotine still less so (1 in 1000). Narceine is more soluble than morphine, while the resin, caoutchouc, etc., are insoluble, though certain gummy matters pass into solution.

"Alcohol dissolves free morphia, as well as the acetate and meconate. The other alkaloids of opium, as also the resin and caoutchouc, are dissolved by alcohol.

"Amylic alcohol dissolves all the alkaloids of opium, if in a free state. The resin is also slightly soluble in amylic alcohol.

"Ether, benzene and carbon disulphide dissolve about 0.05 per cent. of free morphia, and the other free alkaloids of opium more readily. These solvents also dissolve the caoutchouc, but not the resin.

"Acids dissolve all the alkaloids from opium, together with the resin.

"Fixed alkalies used in excess dissolve morphine freely, while narcotine remains insoluble. Lime water dissolves morphine, but is a solvent for narcotine only in presence of morphine. The resin of opium is partly soluble in alkalies.

"Ammonia dissolves morphia sparingly, narceine and codeine readily, while the other alkaloids and the resin of opium are insoluble.

"From the foregoing statements, the arrangement of which is mostly due to Mr. E. L. Cleaver,[1] it follows that an aqueous solution of opium will contain meconate of morphine and other alkaloids, calcium salts, meconic acid, extractives, and resinous matter dissolved by the free acid present.

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[1] Year-Book of Pharmacy, 1876, p. 502.

"An alcoholic solution will contain, in addition to the above, free narcotine, caoutchouc, fat and resin.

"Opium which has been exhausted with water still retains a bitter taste; but this is probably due to narcotine, as it is removed by carbon disulphide, benzene or ether, in which morphine and its salts are insoluble. If the aqueous solution be distinctly acid, water may be trusted to dissolve the whole of the morphia from opium. In some processes of assaying opium the sample is subjected to a preliminary treatment with benzene or ether to remove narcotine, caoutchouc and coloring matter. By this means the subsequent exhaustion with water is much facilitated and a purer solution of morphine is obtained.

"In presence of much narcotine, morphine is soluble in benzene, but this is not true of the meconate or other *salts* of morphine. Hence there is no loss of morphine on extracting opium with benzene. Meconate of morphia is, however, freely soluble in a mixture of alcohol and chloroform, but the simultaneous presence of ether prevents its solution more or less completely. . . . .

"The ash of opium is readily determined by igniting a weighed quantity of the sample. The residue should not exceed 8 per cent.

"An aqueous solution of opium should give a red coloration with ferric chloride. The production of a black or blue-black coloration or precipitate will be due to tannin, which is not a normal constituent of opium.

"Genuine opium contains no starch, and hence, on boiling with water the residue insoluble in cold water, the solution obtained should give no blue coloration with solution of iodine.

"Sand, stones, bullets and other make-weights are sometimes met with as adulterants of opium. Sugar, gum tragacanth, pulp of apricots and figs, pounded poppy capsules, etc., are also employed for the sophistication of opium."

Of the many processes published for the estimation of morphia in opium, none have proved thoroughly successful and easy of accomplishment. In an article by Dr. E. R. Squibb, published in *Ephemeris*, Jan., 1882, is found a full account of a process used by him, and based upon one published by Prof. Flückiger some two years previous. The reader is referred to the article for the full text of the description, but the essential points are described below. The modifications of the original process introduced by Dr.

Squibb, though slight, have great value, because they lead to a thorough exhaustion of the opium and a better crystallisation of the morphia.

Those analytical processes which depend on the use of lime and on the use of an aliquot portion of the filtrate are unsatisfactory, because they do not thoroughly exhaust the opium; because the discarded portion is richer in morphia than the aliquot portion taken; and, lastly, because the volume of liquid used is too large to allow of the full separation of the morphia. These points were examined by Dr. Squibb, who found in an opium of known strength that the first portion of the solution gave 0.544 gram of morphia, the discarded portion gave 0.595 gram, and the two together did not account for the total amount of morphia present by about one per cent. This loss of morphia was found to be due to the large volume of solution used for the precipitation. A test made by myself on this point gave the following results: 10.18 grams of an opium, which gave, by the process hereafter to be described, 11.76 per cent. morphia, was thoroughly exhausted, and the filtered solution evaporated to 100 cc. The requisite amounts of alcohol, ether and ammonia were added. The precipitate obtained weighed 1.020 grams, equal to 10.00 per cent. The filtrate from the crystals was evaporated to 25 cc. and the requisite amounts of alcohol, ether and ammonia added, and a further precipitate of morphia weighing 0.155 gram was obtained, equal to 1.52 per cent. The total amount found was, therefore, 11.52 per cent. In a pure salt of morphia this effect of dilution is not so important. A crystallised sulphate of morphia, which, if pure, should contain 75.2 per cent. morphia, was dissolved and the morphia crystallised from a total volume of 120 cc. of solution. The crystals obtained equalled a percent. of 74.31. On evaporation of the filtrate to 25 cc., and recrystallisation, 0.20 per cent. more was obtained, giving a total of 74.51 per cent. morphia.

Trials made to test the accuracy of using an aliquot portion of the solution gave results too discordant to be of any service. In one case I obtained 10.63 per cent. instead of 11.76 per cent., the actual amount in the opium.

As regards the accuracy of the process about to be described, the following results may be of interest: A lot of opium, very uneven in quality, was sampled by one of our men, and I made the analysis, obtaining—water, 24.30; morphia, 11.75 per cent. Three months afterwards the same lot was re-sampled by myself and one of our men, and the resulting sample analysed by me, in duplicate, using different weights of opium for each analysis. The results obtained were—water, 24.70; morphia, 11.70 and 11.82; average, 11.76 per cent. Other results of duplicate tests showing the same agreement might be given if necessary.

Sampling.—The process of sampling and the preparation of the sample are of great importance, as, on account of the varying quality of the lumps of commercial opium, it is very unlikely that any two lumps will be of the same strength. About every tenth lump in a case is sampled by cutting a cone-shaped piece from the middle of the lump, with an ordinary pocket-knife. From the side of this cone a small strip is taken, and the cone returned to its place in the lump. These separate strips are kept in a tin box until the sampling is finished, care being taken that they do not lose moisture by exposure.

Preparation of the Sample for Analysis.—The sample, composed as it is of many small pieces, is treated as follows: A slab of glass or stone about two feet long is provided, though a small board of hard wood will answer. On this the mass of samples is rolled with the hands, until it is worked into a long, thin roll. This is doubled upon itself and rolled again, re-doubled and re-rolled, and so on until a section cut anywhere from the roll shows a perfectly homogeneous surface. The ease with which this is done depends upon the condition of the sample; a moderately dry sample—that is, with 10 to 12 per cent. of water—will roll out very easily without sticking to the hands, while a wetter one will give some trouble; but with care the sample can be made perfectly uniform in so short a time that no loss of moisture will take place. The sample when prepared is wrapped in tin foil, and placed in a suitable box or bottle to be kept for analysis.

If the sample be hard and dry, and cannot be mixed by the above method, break it up coarsely, take an average portion for moisture, and dry in the water bath an average of the remainder, until it is possible to grind it in a mortar to a sufficiently fine powder. Determine the moisture and the morphia in the prepared sample. Then, by calculation, the result is reduced, first, to the amount present on a dry basis, and then to that present in the original sample. If the sample for analysis is powdered opium, no difficulty will occur in getting a fair average sample.

Moisture.—Two separate portions of the average sample, from 6 to 8 grams each, are weighed and dried at 100° C. From samples prepared as above described, duplicates for moisture will agree very closely. For example:

1	24.70	23.13	22.90	20.30	17.90	20.60
2	24.70	23.40	22.70	20.60	17.50	20.70
Average,	24.70	23.26	22.80	20.45	17.70	20.65

Determination of the Morphia.—Weigh off a portion of the average sample, using about 10 grams, noting the exact weight of the portion taken.

"Put the weighed portion into a flask or common wide-mouthed bottle of 120 cc. capacity, fitted with a good cork. Add 100 cc. of water, distilled by preference—but this is essential only when common water contains an unusual amount of inorganic matter—and shake well. Allow it to macerate over night or for twelve hours, with occasional shaking, and then shake well and transfer the magma to a filter of about 10 centimeters = 4 inches diameter, which has been placed in a funnel and well wetted. As it is the shaking which accomplishes the object here in view, rather than the standing, the time of maceration can be easily shortened even to three hours, if the shaking be frequent and active."[1]

Instead of using a flask or bottle I place the weighed portion in a strong beaker, add 100 cc. water, and then, with a glass rod fitted at the end with a piece of thick rubber tubing, I rub and break up the lump of opium, until in a short time it is thoroughly disintegrated. It is best to let the opium stand some hours in order that the morphia be thoroughly extracted. In test assays it was found that if the solution were filtered off as soon as the lump of opium was broken up and no more dark, soft portions were seen, the amount of morphia obtained was less than the actual amount present. Duplicates made in this manner—by filtering as soon as the dark soluble portions were dissolved—did not agree; but by repeating the operation and allowing the opium to digest over night, the duplicates, made with different amounts of opium, agreed exactly in the amount of morphia obtained. The beaker is covered with a watch glass and placed where no ammoniacal vapors will affect it, although, as the water solution is acid from the organic acids present in the opium, no precipitation of morphia will take place until this acidity be neutralised.

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[1] Ephemeris **1**, 15.

I learn from Dr. Squibb that he has lately adopted the plan of adding a few drops of sulphuric acid to the water used for the exhaustion of the opium. The solution is kept slightly acid, and the extraction of the morphia seems to be thereby facilitated.

"As rare exceptions, some powdered opiums will be found which, through natural conditions, give a magma with water which will not filter, or filter so very slowly that the water solvent becomes impracticable. When this is discovered the magma is thrown away and a fresh portion of powder is taken. Wash this by agitation in the bottle with 30 cc. of ether (sp. gr. .728), transfer it to a filter, rinse the bottle with 20 cc. more of ether, and pour this onto the opium in the filter. When this has passed through, wash the filter and opium with 10 cc. more ether applied drop by drop around the edges of the filter and on the surface of the opium. Then dry the powder on the filter and use it as in the case of opium, which does not need to be first washed with ether.

"Opium which is adulterated, or standardised by admixture with dextrine, gums, sugar or glucosides, yields an impracticable magma with water, and ether-washing to such does little or no good. All such samples have to be exhausted with an alcoholic solvent. If not much adulterated a mixture of equal measures of alcohol (sp. gr. 0.820) and water will answer best, but generally a mixture of two measures of alcohol (sp. gr. 0.820) with one measure of water is to be used, instead of water alone, for the exhaustion, and as this mixture is not as good a solvent for the morphia salts in the opium as water, more of it is required, and the washing and percolating should be carried to 250 cc. of solution from the 10 grams of opium. The process after exhaustion is the same as where water is used as the solvent."[1]

Filtering off the Aqueous Solution of Morphia.—Filter off the solution into a graduated cylinder, and wash the filter and residue with water applied from a wash bottle until the filtrate measures about 120 cc.; set this strong solution aside, and return the residue to the bottle or beaker by means of a small spatula; add 30 cc. of water, and mix or shake well, and filter this solution through the same filter. Again return the residue and treat with 20 cc. of water and filter, and finally repeat the treatment with 20 cc. more. By the use of the rubber-tipped rod and a beaker it is possible to so press out the water from the insoluble residue that the above treatment will exhaust 10 grams of any opium. The water is much more thoroughly obtained from the residue than by using several more washings without pressure. It is best to let the several washings stand on the residue for ten minutes or so before transferring to the filter. These washings are received in a beaker, and are the first portion to be evaporated.

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[1] Ephemeris 1, 15.

Evaporation of the Aqueous Solution of Morphia.—The second portion of the solution, the washings, measuring about 70 cc., is placed in a porcelain capsule of 6 to 8 inches diameter, and evaporated over a water bath at a heat below boiling. By using a broad, shallow dish this evaporation takes little time, and the danger of injury to the alkaloid is reduced to a minimum. Evaporate to about 25 cc. and then add the first portion of the solution, washing out the cylinder with a little water from the wash bottle, and evaporate the whole to about 25 cc. Cool the capsule and contents and add 5 cc. of alcohol (sp. gr. 0.820), and stir until a uniform solution is obtained. If a precipitate is obtained, as sometimes happens, it is not necessary to filter, as this precipitate is removed in a subsequent treatment, and is not reckoned as morphia.

Transferring to the Crystallising Flask.—Pour the solution into an Erlenmeyer flask fitted with a good velvet cork, using a flask of about 2 inches diameter at the bottom and 5 inches high, and wash the capsule with about 5 to 10 cc. of water from the wash bottle. I find that the quantities of water for washing and for the precipitation of the morphia may be slightly greater than those recommended by Dr. Squibb, without injury to the analysis. Add 5 cc. more of alcohol, and mix the liquids thoroughly by rotating the flask, and not by an up and down movement. Then add 30 cc. ether and again mix well by rotating.

"This shaking together first of the watery solution and alcohol causes the alcohol to combine with the water before the ether is added. The ether then added, the second shaking saturates the watery solution and combined alcohol with ether, and then the mixture is ready for the precipitation of the alkaloid under the most favorable condition."[1]

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[1] Ephemeris **1**, 17.

Precipitation of the Morphia.—Add 4 cc. of ammonia solution of 10 per cent. (sp. gr. 0.960), wet the cork with ether, and insert at once into the flask. Shake the flask *strongly* with an up and down motion until the crystals begin to separate. This will occur in a moment or two if everything has been properly carried out. Then set the flask aside for twelve hours, or over night, to complete the crystallisation. By this vigorous shaking the crystals are obtained in a fine granular condition, easily washed and separated from the flask.

Filtering off the Morphia.—" Pour off the ethereal stratum from the flask as closely as possible onto a tared filter of about 10 centimeters = 4 inches in diameter, well wetted with ether. Add 20 cc. of ether to the contents of the flask, rinse round without shaking, and again pour off the ethereal stratum as closely as possible onto the filter, keeping the funnel covered. When the ethereal solution is nearly all through, wash down the edges and sides of the filter with 5 cc. of ether, and allow the filter to drain with the cover off. Then pour on the remaining contents of the flask, and cover the funnel. When the liquid has nearly all passed through, rinse the flask twice with 5 cc. of water each time, pouring the rinsings with all the crystals that can be loosened onto the filter, and dry the flask in an inverted or horizontal position, and when thoroughly dry, weigh it. Wash the filter and crystals with 10 cc. of water applied drop by drop to the edges of the filter. When drained, remove the filter and contents from the funnel, close the edges of the paper together, and compress it gently between many folds of bibulous paper. Then dry it at 100° C., and weigh it. Remove the crystals of morphia from the filter, brush it off, and re-weigh it to get the tare to be subtracted. The remainder, added to the weight of the crystals in the flask, will give the total yield of morphia, in clean, distinct, small, light brown crystals.

" Take a small portion of these crystals, rub them into very fine powder, and weigh off 0.1 gram. Put this in a large test tube fitted with a good cork, and add 10 cc. of officinal lime water. Shake occasionally, when the whole of the powder should dissolve. (Absence of Narcotine: Flückiger.)

" . . . This process, according to the skill and care with which it is managed, will give uniform results to within two or three-tenths of a percent. Adulterated opiums are much more difficult to assay, and yield crystals which are always darker and less clean, and therefore the results are almost always too high. Poor opiums, on the other hand, are very easy to assay, and usually give very light-colored, clean morphia. The results here are liable to be too low, because, when the quantity of morphia is small, the alcohol and ammonia used are proportionally too large, so that much morphia may be retained in the mother-liquor. Therefore, when the morphia comes out very white and in small proportion, the assay should always be repeated, evaporating the solution to 10 grams instead of 20, and adding 5 cc. of alcohol instead of 10, and 2.5 or 3 cc. of ammonia instead of 4. . . .

"The above process is very easily applicable to the assay of such preparations of opium as the tincture, deodorised tincture and compound solution. For the assay of these:

"Take of the liquid preparation 120 cc. Evaporate at a low temperature to 10 grams, and from this point proceed exactly as in the above process, using, however, 5 cc. of alcohol instead of 10, and 2.5 to 3 cc. of ammonia instead of 4."[1]

In following out the above plan of Dr. Squibb, several difficulties are met with. The amount of ether recommended for washing is so small that in some cases where the operation of filtering proceeds with great difficulty, much of the ethereal solution is evaporated from the edges of the filter paper, leaving its contents behind, and these are not thoroughly washed out by the subsequent treatment. The amount of water, also, is too small to allow of perfect washing.

Washing Solutions.—In order to obviate these difficulties I have adopted a plan for which I am indebted to a paper published by E. F. Teschemacher, F. C. S., etc., in the *Chemical News*, Vol. 35, p. 47. The first solution, which he calls "*Morphiated Spirit*," is made by mixing one part of ammonia solution, sp. gr. 0.880, with twenty parts of alcohol, and digesting in this mixture, for several days, a large excess of morphia. The clear solution will contain 0.33 per cent. of morphia. The second solution, called "*Morphiated Water*," is water saturated by long shaking with morphia. The filtered solution contains 0.04 per cent. morphia.

By washing with these solutions the extractive matter is completely removed from the filter paper and crystals of morphia. I prefer to use balanced filter papers, of 4½ inches diameter. The solution is run through one of these, and, by means of the thorough washing with the solutions above described, the two papers are left, at the end of the operation, ready for weighing against each other as at first. I pour off the ethereal stratum through the filter as above described, and then wash several times with 10 cc. of ether, rinsing the flask around without shaking, and letting settle for a few minutes. Even if a small amount of the ethereal residue is left upon the paper by evaporation, it is immaterial, as in the subsequent treatment this is removed. A small syphon is advantageously used to draw off the ethereal solution from the Erlenmeyer flask, but if an attempt be made to syphon off the ethereal washings, it will be found that the bubbles formed in the ether collect in the tube of the syphon and prevent its action, so that it is better to wash by decantation. If some of the aqueous solution pass onto the filter with the ether, it is of no importance. The washing with ether is followed, first, by a thorough washing with the "*Morphiated Spirit*," thus removing all the coloring matter and resin soluble in this menstruum, and then by a thorough washing with the "*Morphiated Water*," until the filtrate comes through colorless and the paper shows by its color that all the extractive matter is removed. By the use of the Erlenmeyer flask it is possible to remove with the rubber-tipped rod all the crystals from the flask, so that no drying and weighing of the flask is needed. After the washing with the "*Morphiated Water*" the filter is left to drain for a few minutes in the funnel, and two washings of 10 cc. each with the "*Morphiated Spirit*" are given. This removes the bulk of the water from the paper and crystals. Let drain for a few minutes, keeping the funnel covered with a watch glass, and then wash twice with 10 cc. each time of ether. This will remove any narcotine which may have been left from the evaporation of the ethereal solution at the beginning of the operation. The paper and contents are thus left in a condition to be rapidly dried. Let the filter and its contents stand exposed for a few minutes, and then dry it at 100° C. and weigh. Twenty minutes or half an hour's drying is usually sufficient.

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[1] Ephemeris **1**, 17, 20.

On account of the removal of the water it is possible to dry the filter and its contents in a short time at a much lower temperature than 100° C., but as it is easier to employ this heat, and no decomposition of the morphia crystals occurs, I use it. A precipitate of morphia crystals was dried for two hours at 60° C., yielding a weight of 1.306 grams. It was further dried for three hours at the same heat, and then weighed 1.305 grams; still further dried for two hours at 100° C., it became 1.301 grams.

The mother-liquor, together with the first washings of ether and "*Morphiated Spirit,*" is put in a flask, 3 cc. of ammonia added, and the corked flask is set aside over night in order to see if a further crystalline precipitate of morphia occur. If the solution is left exposed in an open beaker, amorphous flakes will settle out, consisting chiefly of resinous matter, very different from the heavy crystalline deposit of morphia.

Having thus obtained the weight of the crystalline precipitate, it is still necessary to further purify it before the final calculation is made for the percent. The precipitate of morphia obtained by Dr. Squibb's process contains insoluble matter, resinous and other organic matters soluble in alcohol, and meconate of lime, the latter constituting about 25 per cent. of the impurities present. The average amount of the impurities present in the crystals obtained by his process is 8 per cent. of the weight of the crystals. The meconate of lime extracted by the acid solution of the opium is retained in solution until the addition of the ammonia, when it is precipitated with the crystals of morphia, and remains with them until the final weighing. The resinous and other organic matters, insoluble in water, but soluble in alcohol, are not thoroughly removed with the limited washing given in his process, and no provision is made for their subsequent removal. The thorough washing with "*Morphiated Spirit*" which I employ takes out these substances, and the subsequent treatment with "*Morphiated Water*" removes those insoluble in alcohol, so that the chief impurity present in the crystals of morphia obtained by my modification of the process is meconate of lime, together with some organic matters insoluble in water and alcohol.

Purification of the Precipitate.—After drying and weighing the crystals they are carefully rubbed or brushed from the filter, the latter being then placed in a funnel and preserved with its balanced paper for future use. The precipitate is treated in a small beaker with hot alcohol of 95 per cent. This dissolves all the morphia, leaving the insoluble organic matter and meconate of lime. The hot alcoholic solution is run through the filter which contained the morphia, the small portion of the crystals remaining on the paper being thus drenched with hot alcohol and the morphia dissolved. This treatment with hot alcohol is continued until all the morphia is dissolved. This extraction with alcohol may be done in a Soxhlet's apparatus, if desired. The filter is then dried with its balanced paper and the amount of residue obtained. This is subtracted from the original weight of the precipitate, and the remainder calculated into the percent. of morphia. The alcoholic solutions of morphia are placed in a bottle and left to deposit the excess of morphia, and the alcohol, saturated with morphia, is used for the preparation of the "*Morphiated Spirit*" as before described. Meconate of lime I found to be perfectly insoluble in boiling alcohol. A long treatment with this solvent failed to dissolve enough meconate of lime to give a trace of color with ferric salts.

The composition of the morphia crystals, on which the calculation for the percent. is based, is $C_{34}H_{19}NO_6 + 2Aq$, containing 5.94 per cent. of water of crystallisation. At 120° C. the water is expelled, and at a higher temperature the crystals become carbonised.

The following is a brief summary of my process as practised in our laboratory.

1. *Sampling.*—By taking a portion of every tenth lump in a case.

2. *Preparation of the Sample.*—By thorough mixing of the small samples obtained, either by kneading and rolling, or by drying the sample, with previous estimation of the water.

3. *Extraction of the Morphia.*—Weigh off about 10 grams, noting the exact weight taken; treat with 100 cc. of water in a suitable vessel, macerate, let stand over night, filter and wash, making two portions of the filtrate. Evaporate on a water bath, first the weaker portion, about 70 cc. of solution, then add the stronger portion, and evaporate all to 25 cc.; add 5 cc. of alcohol and stir until all is dissolved.

4. *Precipitation of the Morphia.*—Transfer the solution to a suitable flask, add 5 cc. more of alcohol, mix; then add 30 cc. of ether, mix; then add 4 cc. of a 10 per cent. solution of ammonia, sp. gr. 0.960. Shake violently until the crystals form, and let stand over night.

5. *Filtration of the Morphia.*—Filter off, first, the ethereal solution and wash well with ether. Then filter the aqueous solution, and wash, first with "*Morphiated Spirit*," then with "*Morphiated Water*," then with "*Morphiated Spirit*," and finally with ether. Dry at 100° C. and weigh, using balanced papers.

6. *Purification of the Morphia.*—Treat the impure precipitate

with hot alcohol until all the morphia is dissolved, wash thoroughly with hot alcohol, dry and weigh the insoluble residue. Subtract this from the first weight of the precipitate to get the amount of morphia present.

7. *Statement of the Result.*—Give the percentage of moisture present at 100° C., and of morphia, both on a wet and a dry basis, in terms of crystallised morphia, $C_{34}H_{19}NO_6 + 2Aq$, dried at 100° C.

WASHING SOLUTIONS.

a. "*Morphiated Spirit.*"—This is made by mixing one part of ammonia solution, sp. gr. 0.880, with twenty parts of alcohol and saturating with morphia. The filtered solution contains 0.33 per cent. of morphia.

b. "*Morphiated Water.*"—This is made by saturating water by long shaking with excess of morphia. The filtered solution contains 0 04 per cent. of morphia.

c. *Ether.*—Called stronger ether, sp. gr. 0.728 at 15.5° C.

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ON THE ACTION OF CHLORINE UPON PYRIDINE.

[PRELIMINARY COMMUNICATION.]

BY E. H. KEISER.

The action of the halogen elements upon the bases of the pyridine series has been but little studied, and our knowledge of the halogen derivatives of these bases is very imperfect. This is undoubtedly due to the fact that pyridine is one of the most stable of organic compounds, and its substitution products can only be obtained with the very greatest difficulty. The first work in this direction was undertaken by Anderson[1] in 1857. Having succeeded in isolating a quantity of pyridine from the bases which accompany it in bone oil, he endeavored to throw some light upon its constitu-

[1] Liebig's Annalen der Chemie **105**, 340.

tion by studying its decomposition products. He tried, in the first place, the effect of oxidising agents upon pyridine, but found that it remained undecomposed when boiled with concentrated nitric acid, and that even a boiling solution of chromic acid produced no change. He then studied the action of the halogens upon pyridine, but found that in this way no definite results could be obtained. In regard to the action of chlorine upon pyridine, he observed that when a current of this gas is conducted into an aqueous solution of pyridine, the chlorine is rapidly absorbed; the solution becomes dark brown in color, and acquires a peculiar irritating odor. If caustic potash be thereupon added to the liquid, a dark brown resin is formed and the solution again has the odor of pyridine. He also noticed that if an excess of pyridine be poured into a large vessel containing chlorine, and if the pyridine be rapidly distributed upon the walls of the vessel to avoid an increase of temperature, then it does not become dark brown in color, but is converted into a mass of radiating crystals. These crystals dissolved readily in water, but at the same time a small quantity of a snow-white powder remained undissolved. When dried, the white powder had an odor resembling that of bleaching powder. None of the substances obtained by Anderson were analysed, and, therefore, no information was obtained in regard to the constitution of pyridine. He also treated pyridine with bromine and iodine, but in these cases the results were not more satisfactory than in the case of chlorine.

From an examination of the literature on this subject it appears that since these experiments of Anderson no other attempts have been made to study the action of chlorine upon pyridine. Two chlorine derivatives[1] of pyridine have been described, but these have been obtained by indirect methods, and not by the direct action of chlorine upon pyridine.

Hofmann[2] has studied the action of bromine upon pyridine, and found that an orange-yellow crystalline addition product is formed when a hydrochloric acid solution of the base is treated with bromine. The addition product is unstable, being decomposed when heated. It probably has the formula $C_5H_5NBr_2$. If this crystalline addition product be heated to a temperature of 200° in sealed glass tubes, some bibrompyridine, $C_5H_3Br_2N$, is formed.

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[1] Berichte der deutschen chemischen Gesellschaft **14**, 1154; **15**, 1179; **17**, 594.

[2] *Ibid.* **12**, 990.

Hofmann also found that bibrompyridine is formed by heating pyridine hydrochlorate with bromine in sealed tubes, in the proportion of one molecule of pyridine hydrochlorate to two molecules of bromine.

The present investigation was undertaken with the intention of studying more thoroughly the action of the halogen elements upon the bases of the pyridine series. The object was to determine the conditions under which addition and substitution products may be formed, and by a study of these derivatives to throw some light upon the constitution of the bases themselves. The investigation began with the study of the action of chlorine upon pyridine. Preliminary experiments soon showed that when chlorine comes in contact with an aqueous solution of pyridine the effect is totally different from that which is produced when chlorine acts upon pure pyridine.

If a current of dry chlorine be conducted into a vessel containing pyridine, which is free from water, the gas is rapidly absorbed and heat is evolved. The pyridine soon becomes yellow in color, then red, and afterwards dark red. Crystals then begin to separate, and finally, if the supply of chlorine is continued, the liquid will be completely converted into a brownish-black solid mass. This black solid is very deliquescent in the air. It dissolves readily in water and alcohol; but it is insoluble in ether, benzene and acetone. The black solid was heated in a retort; it melted below 100°, and on raising the temperature an oily liquid distilled over at 116°. The heating was continued, and at 130° a white crystalline solid condensed in the neck of the retort. These crystals were removed, and on heating still higher the contents of the retort bumped violently; nevertheless a considerable quantity of a yellow waxy solid condensed in the receiver.

An examination of the distillation products showed that the liquid which came over at 116° was unchanged pyridine. It contained in solution some of the crystalline solid which distilled at 130°. This was separated by diluting the pyridine with a large quantity of water. On standing, the solution contained a quantity of crystalline needles. The crystals thus obtained, as well as those which condensed in the neck of the retort, were purified by repeated recrystallisation from alcohol. When pure, they present the appearance of long, slender white needles, which melt at 72°. They dissolve readily in pyridine and alcohol, but are insoluble in water. The substance is very stable in the air; it does not deliquesce, and has an agreeable aromatic odor. To determine the nature of this derivative of pyridine a portion was dissolved in alcohol, and the solution was treated with platinum tetrachloride. A beautiful, yellow, crystalline double salt was obtained, which differs very much in appearance from pyridine platinum tetrachloride. An analysis of the salt showed that it corresponded in composition with the double salt of a bichlorpyridine.

.1054 gram of the salt gave .0291 gram metallic platinum = 27.60 per cent.

$(C_5H_3Cl_2NHCl)_2PtCl_4$.	Calculated.	Found.
Pt	27.61	27.60

It seemed, therefore, highly probable that the crystalline substance was the hydrochlorate of bichlorpyridine, and a determination of chlorine confirmed this view.

.1370 gram substance gave .3154 gram AgCl = 56.93 per cent. chlorine.

$C_5H_3Cl_2NHCl$.	Calculated.	Found.
Cl	57·6	56·93

The quantity of substance obtained was so small, however, that, after the preceding experiments had been made, there was not sufficient material remaining for making a combustion of the compound. I shall endeavor to prepare it in larger quantity, and hope to be able to study it more thoroughly.

The yellow waxy solid, which was obtained as the last distillation product from the black mass, was purified by redistillation. It boiled at 218°, and the larger quantity passed over at 219°. It can not be distilled without decomposition, and after each distillation a quantity of carbon remained in the retort. The vapor of the compound attacks and destroys cork. The solid substance is extremely deliquescent in the air, and dissolves readily in alcohol. To determine whether it was an addition or substitution product of pyridine, a portion was dissolved in water, and the solution was treated with platinum tetrachloride. A red crystalline double salt was obtained, which possessed all the properties of pyridine platinum chloride.

.1401 gram salt gave .0475 gram metallic platinum.

$(C_5H_5NHCl)_2PtCl_4$.	Calculated.	Found.
Pt	34·31	33·95

It appeared, therefore, that the waxy, deliquescent solid was an addition product of chlorine and pyridine. An analysis of the compound gave the following result:

I. .2691 gram substance gave .5131 gram CO_2 and .1223 gram $H_2O = 52.0$ per cent. C and 4.68 per cent. H.

II. .0965 gram substance gave .1206 gram $AgCl = 30.89$ per cent. Cl.

These results indicate that the addition product has a composition which may be represented by the formula C_5H_5NCl.

	C_5H_5NCl.	Calculated.	Found.
C	59.85	52.39	52.00
H	5.00	4.37	4.68
N	14.01	12.28	...
Cl	35.37	30.96	30.89
	114.23	100.00	

A determination of the vapor density of the compound was made at a temperature of 250°. The specific gravity was found to be 2.49, a result which indicated that at that temperature the compound had suffered dissociation.

Briefly stated, the results obtained are as follows: When dry chlorine gas acts upon pyridine the gas is rapidly absorbed, heat is evolved, and the liquid is converted into a black solid mass. This black solid consists chiefly of an addition product of chlorine and pyridine, whose composition may be represented by the formula C_5H_5NCl. There is also present in the black solid some unchanged pyridine and a small quantity of bichlorpyridine hydrochlorate, $C_5H_3Cl_2NHCl$. The latter substance crystallises in beautiful needle-shaped crystals, and is a very stable compound.

If, however, the pyridine is diluted with water and chlorine allowed to pass through the solution, then the action is totally different from that which has just been described.

Twenty cubic centimeters of pyridine were diluted with an equal quantity of water, and a current of chlorine was passed into the solution. The gas was rapidly absorbed, the liquid became warm and soon acquired a dark red color. After a time small bubbles of gas were evolved from all parts of the liquid, and this evolution of gas increased and continued for a long time after the current of chlorine had ceased. An examination of the gas showed that it consisted of a mixture of nitrogen and carbon dioxide. The solution of pyridine was then diluted with water, and a small quantity of a snow-white, flocculent precipitate was obtained. It was removed by filtration; and, after drying, it was found to have an odor resembling that of bleaching powder. A further examination of its properties showed it to be identical with the white powder obtained by Anderson.[1] A qualitative test showed that the white powder contained nitrogen. The alcoholic solution of the white substance was treated with platinum tetrachloride, and a dark red, crystalline, platinum double salt was obtained. After purification this salt resembled in its properties the double salt of pyridine and platinum tetrachloride.

When analysed .1132 gram of the salt gave .0388 gram metallic platinum = 34.28 per cent.

$(C_5H_5NHCl)_2PtCl_4$.	Calculated.	Found.
Pt	34.31	34.28

The white substance must therefore be an addition product of pyridine. From its method of formation, and its unstable character, it seems probable that the substance is a hypochlorite of pyridine, C_5H_5NHOCl. The composition of this white substance will be studied more thoroughly in a future investigation.

It seems probable, then, that when chlorine is passed into an aqueous solution of pyridine, pyridine hypochlorite is formed, and the evolution of nitrogen and carbon dioxide is due to the decomposition of this compound. Experiments were made with alkaline hypochlorites and aqueous solutions of pyridine. It was found, in every case, that, whenever pyridine was heated with solutions of hypochlorites, nitrogen gas was evolved. Under certain conditions this decomposition of pyridine by hypochlorites took place very rapidly. In one experiment 50 grams of caustic potash and 5 grams of pyridine were dissolved in 300 cc. of water, and chlorine was passed into the solution. In a short time decomposition began, and, as the current of chlorine was not instantly stopped, the evolution of nitrogen became so rapid that the larger portion of the liquid was thrown violently out of the flask. In another experiment, which was made with the same quantity of materials, the nitrogen was evolved with explosive violence, and the flask containing the solution was shattered. If the temperature of the flask containing the solution of pyridine and alkali is kept down by surrounding it with cold water, the decomposition takes place slowly, and the nitrogen gas is evolved much more regularly. Several grams of pyridine were decomposed in this way, and an examination of the liquid showed that the decomposition products, beside the nitrogen and carbon dioxide, were chloroform and chloracetic acid. The chloroform was removed from the liquid by distillation. It was recognised in the distillate by its odor, by its reducing action upon Fehling's solution, and by its formation of isocyanphenyl with aniline and alcoholic potassa. The liquid, from which the chloroform had been removed, was evaporated to dryness and extracted with absolute alcohol. The alcoholic solution was treated with silver nitrate, and, on standing, a salt separated which blackened in the light. Although it was too impure for analysis, it possessed all the properties of silver dichloracetate. When heated on platinum foil the salt deflagrates, and with alcohol and sulphuric acid the ethyl ester is obtained, which may be readily recognised by its pleasant odor.

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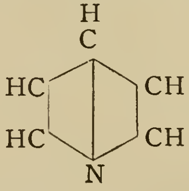
[1] Liebig's Annalen der Chemie **105**, 340.

As a result of these experiments it appears, therefore, that when pyridine is decomposed in an aqueous solution by chlorine, or by hypochlorites, there are formed, beside nitrogen and some carbon dioxide, chloroform and dichloracetic acid.

While in recent years pyridine and pyridine derivatives have been built up synthetically from simpler substances, no experiments have hitherto been described in which the pyridine molecule has been decomposed into simpler organic compounds. The fact that chloroform, chloracetic acid and nitrogen are so easily obtained as the decomposition products of pyridine may perhaps be regarded as a confirmation of the hypothesis of Riedel[1] in regard to the constitution of the pyridine molecule. If we assume the formula of pyridine to be , then it is not difficult to account for the formation of chloroform and chloracetic acid, for it may be supposed that decomposition takes place as is indicated by the dotted lines.

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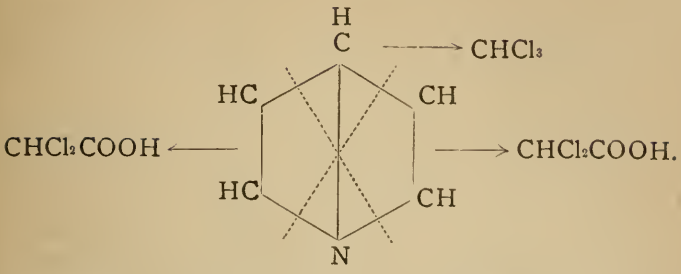
[1] Berichte der deutschen chem. Gesellschaft **16**, 1609.



If, however, we assume Körner's ring formula as representing the constitution of pyridine, then we would naturally expect to find much more complicated decomposition products—that is, compounds which contain more than two carbon atoms.

This investigation will be continued in the directions indicated, and will include a study of the action of the halogen elements upon the other members of the pyridine series of bases.

BRYN MAWR, PA., *August*, 1886.

ABSORPTION TUBES FOR THE ESTIMATION OF CARBONIC ACID IN ATMOSPHERIC OR GROUND AIR.

BY THOMAS C. VAN NÜYS.

Having employed Pettenkoffer's absorption tubes[1] in connection with an apparatus, described and illustrated in this Journal, Vol. 8, No. 3, in estimating carbonic acid in the air, I found that the Pettenkoffer tubes yielded results too high and subject to greater variation than those obtained with my apparatus. This I concluded was due to the absorption of carbon dioxide from the air by the baryta after a measured quantity of air had passed through the tubes and before titrating with the oxalic acid solution. To overcome this difficulty I devised the tubes represented in Fig. 1. They were made by Mr. Emil Greiner, 79 Nassau st., New York.

[1] Annalen der Chemie, Suppl. Bd. 2, 23; Zeitschrift für analyt. Chemie 1, 495.

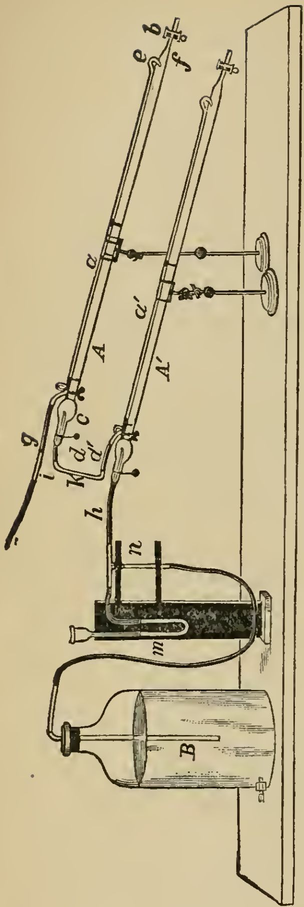


FIG. I.

As each tube is of the same construction, the description of one will answer for both.

Tube *A* from the stop-cock *b* to the bulb *c* is 90 cm. in length, and its external diameter is 16 mm. and internal diameter about 11 mm. The outside diameter of the enlarged portion or bulb *c* is 4 cm. The capacity of the tube from the stop-cock to the bulb is 96 cc. The stopper *d* fits with a ground surface in the tube, and is drawn out at either end. A rubber tube fits over the distal end, and the other end is bent and drawn out to a certain extent. This extremity of the stopper is therefore directed towards the upper part of the surface of the enlarged portion of the tube. Passing through the stopper longitudinally is an opening 4 mm. in diameter, except at its proximal extremity, where the diameter is about 2 mm. The small tube *a* is fastened to the absorption tube by having rubber tubing placed over it in two places and secured by fine cord. Its outside diameter is 6 mm. Within a few centimetres of the stop-cock the tube, after making the curve *e*, enters the absorption tube and is welded with the latter at point of entrance.

In the absorption tube it is drawn out and somewhat curved in its course, so that its extremity *f* is directed towards the centre of the absorption tube. The diameter of the orifice of the tube at *f* is less than 1 mm. At the enlarged portion of the absorption tube the small tube *a* is bent, and terminates nearly opposite and about 5 cm. from the stopper. The aspirator bottle *B* is connected with the absorption tube *A′* by tubing. The manometer *m* communicates with the absorption tube and aspirator bottle by means of

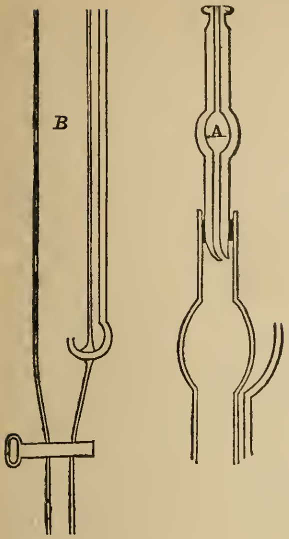


FIG. 2.

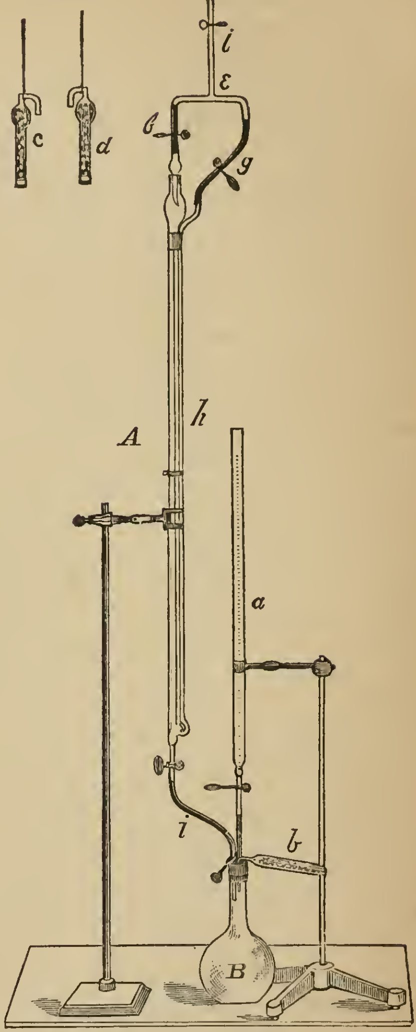


FIG. 3.

the T tube *n*. The construction of the stopper of each absorption tube and the tube *a* or *a′* (Fig. 1) as it terminates in the absorption tube are illustrated in Fig. 2.

Fig. 3 represents one of the absorption tubes connected with the flask *B*. The flask is provided with a rubber stopper having three holes, through one of which a bent glass tube passes, which is connected with the absorption tube by means of a rubber tube. The long tip of the burette *a* passes through the second hole, and through the third hole the bent end of the calcium chloride tube *b* passes. This tube is filled with pumice saturated with a strong solution of sodium hydrate. The calcium chloride tubes *c* and *d* contain soda-lime. The lower end of each tube is closed with a cork stopper having a small perforation, and the soda-lime is secured in place by some cotton in either end. The rubber tube *j*, connected with an aspirator bottle containing water about one metre above the upper end of the absorption tube, is attached to the T tube *e*. Besides showing the plan of the absorption tubes, Fig. 1 illustrates their position and relation to each other when they are being filled with air free of CO_2, and when the process of absorbing the carbonic acid of the air is in progress.

By Fig. 3 the processes of filling, emptying and washing them are illustrated.

The barium hydrate solution I use is made by dissolving about 3.5 grams in 1000 cc. water, and to this solution about 2 grams barium chloride is added to react on any potassium or sodium hydrate that may be present as an impurity. If the solution formed is not clear it should be filtered into a tubulated or aspirator bottle, which, to prevent the ingress of air containing carbon dioxide, is provided with a rubber stopper with which a simple calcium chloride tube is fitted with its drawn-out extremity bent, and the tube filled with pumice saturated with a strong solution of sodium hydrate. The oxalic acid solution used is prepared by dissolving 2.8636 grams pure acid in 1000 cc. water. Solution of oxalic acid of this strength was first employed by Pettenkoffer; 1 cc. of it equals the saturating power of 1 milligram, or 0.5084 cc. carbon dioxide at normal temperature and pressure. To ascertain how much of the oxalic acid solution is required to neutralise 50 cc. of the barium solution, the titrations should be carried on in the absence of air containing carbon dioxide.

To accomplish this the method of F. Schulze[1] may be employed. Into a 100 cc. flask, having been cleaned and dried, a piece of sodium hydrate is suspended by means of a wire. The flask is closed by a stopper, allowed to stand a few hours, when the sodium hydrate is carefully drawn out. A piece of rubber sheet having a small perforation is placed over the mouth of the flask and secured by a rubber band, and into the flask through the small opening in the rubber sheet a few drops of an alcoholic solution of rosolic acid are introduced by means of a small pipette, after which 50 cc. of the baryta solution are introduced from a pipette which has been filled by Pettenkoffer's method, when the tip of a 25 cc. burette containing the oxalic acid solution is introduced through the perforation, and the solution is titrated until the red color of the rosolic acid disappears.

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[1] Zeitschrift für analyt. Chemie 9, 292.

With as great security against the presence of carbonic acid, the flask in Fig. 3 may be employed by having been dried, two or three drops rosolic acid solution introduced, the bent glass tube pushed further down into the flask, the rubber tube attached to a wash bottle containing a strong solution of sodium hydrate, and a U-shaped calcium chloride tube containing soda-lime and cotton, the latter next the flask, and through these the air is drawn into the flask by attaching the end of the calcium chloride tube *b* to an aspirator. When three or four litres of air have been drawn through, the rubber tube is secured by the pinch-cock. Into the free end of the tube filled with water the tip of a 50 cc. pipette filled with the barium solution is introduced, and by loosening the pinch-cock the solution is let into the flask. Some water is introduced in the same way, so as to wash all of the barium solution from the tube, when the solution is titrated with the oxalic acid solution in the burette. When an agreement is reached it is found that from 23.5 to 24 cc. oxalic acid equal 50 cc. of the barium hydrate solution. Both absorption tubes are so connected that when the tube *g* (Fig. 1) is attached to a wash bottle containing a solution of sodium hydrate, and two U-shaped calcium chloride tubes containing soda-lime, and some cotton in the tube next to tube *g*, the absorption tubes can readily be filled with air free of carbon dioxide, but the air should not be drawn through with great rapidity, and the cotton should be in quantity sufficient to arrest any particles of soda-lime that may be separated by the air.

The absorption tubes having been filled with air free of carbon dioxide, the rubber tubes *gi* and *jh* are secured by pinch-cocks. Each absorption tube is filled with the barium hydrate solution, by placing them in position as in Fig. 3. The rubber tube *f* is placed over the bent end of either tube *c* or *d*. The tip of a 50 cc. pipette filled to the mark with the barium solution is introduced into the rubber tube *g*, when the pinch-cocks are removed from the tubes *g* and *f*, and the solution will run through the small tube *h* into the absorption tube, after which from 30 to 35 cc. water are introduced in the same way, when the rubber tube *g* is secured by the pinch-cock; and that the water may pass down from the end of this tube, connection is made with it and tube *d*, when the water will descend by loosening the pinch-cock. Both tubes having been secured by pinch-cocks, the absorption tube is ready for use. The other absorption tube is filled in the same way, and they are connected as before by means of the glass tube *k* (Fig. 1). The tube *l*, through which air passes to enter the absorption tubes, is two or three metres long. It cannot well be dispensed with, as there is great liability of the air becoming charged with an increased quantity of carbonic acid by persons remaining any length of time about the apparatus while air is passing through the tubes. I found this true in several instances. For the same reason the apparatus is placed so that the movement of air; if appreciable, is from the open end of the tube *l* towards the apparatus.

Before passing air through the absorption tubes all rubber tubing making connections is secured by fine iron wire, and to ascertain if the connections are air-tight, all of the pinch-cocks, except the one securing tube *g*, are removed, and by turning the stop-cock of the aspirator bottle, if air ceases to pass through the absorption tubes, and especially after closing the stop-cock of the aspirator, the mercury in the manometer remains stationary, the connections are air-tight. When the pinch-cock securing the tube *g* is opened so that air may enter, it passes through both absorption tubes, and enters the aspirator bottle as the water escapes. By measurement of the latter, taking into account the pressure and temperature, the quantity of air at 0° C. and normal pressure which passed through the tubes is ascertained.

The pinch-cock securing the tube *g* is gradually opened by means of a metallic wedge, so that air may pass through the absorption tube *A* in small bubbles. If they tend to unite to any great extent, or the current is interrupted, the pinch-cock is adjusted so that less air may enter. It will be found necessary to adjust the pinch-cock on the tube in the same way, employing a metallic wedge or a pinch-cock provided with a screw, so as to regulate the size of the bubbles in the absorption tube *A'*. If the operator trust to the adjustment of the stop-cock of the aspirator bottle, liability to failure in securing a correct result is very great, as the air bubbles formed are often large, and some carbonic acid may escape absorption. By passing air through the tubes at the rate of three litres per hour, all of the carbonic acid is absorbed. In nearly all of the estimations made with these tubes eight litres of air were passed through the tubes, requiring about two and a half hours. The temperature of the air, the height of the barometer and of the mercury in the manometer do not receive special attention until near the end of the process, for the reason that should there be changes in temperature or pressure the current of air through the tubes and the flow of water are so regulated that the volume of air in the aspirator bottle at the expiration of two, three or four hours corresponds to the volume of water which had escaped the last moment of the process.

For example, at the expiration of two hours the temperature was 8° C., when four litres of air had entered the aspirator bottle; but at the expiration of the fourth hour the temperature was 12° C., the barometric pressure remaining the same. During the last two hours 4000 cc. air in the aspirator expanded $\frac{4}{273}$ of its volume. $4000 \times \frac{4}{273} = 58.6$. The increase of 58.6 cc. due to expansion by increase of temperature during the process prevented an equal volume of air from entering the aspirator bottle, consequently 58.6 cc. water passed out of the aspirator bottle and was measured, while no air passed through the absorption tubes to supply the place.

In the reduction of the volume of air to normal temperature, taking into account the increased temperature as ascertained at the end of the process, the correction is made. It is at once perceived that if the temperature were reduced during the process, a greater volume of air would pass through the absorption tubes than that occupied by the water from the aspirator bottle. For the same reason, to avoid incorrect results arising from change of temperature or barometric pressure during the process, the aspirator bottle is filled to the stopper. In case the aspirator contained air at the beginning of the process, and a change of temperature or pressure took place during the process, the volume of water measured does not represent the volume of air passed through the tubes at the temperature and pressure at the end of the process without taking into account the expansion or contraction of the air in the aspirator at the beginning of the process. As temperature is a very important factor to be taken into consideration in reaching correct results, the water in the aspirator, before beginning the process, should be about the temperature of the air, and the apparatus is placed so as to be protected from the direct light of the sun, to avoid difference of temperature of the air and water in the aspirator at the end of the process. Preparatory to emptying and washing the tubes the 50 cc. burette *a* (Fig. 3) is filled with the oxalic acid solution. Two or three drops of an alcoholic solution of rosolic acid are introduced into the flask *B*, and it is filled with air free of carbonic acid as above, when the rubber tube *i* is closed by means of the pinch-cock, and its end is filled with water, as well as the glass tube from the glass stop-cock of the absorption tube. The end of the rubber tube is fitted over the glass tube. In this way no air containing carbonic acid can enter the flask. The end of the rubber tube *f* is filled with water from the pinch-cock and fitted over the bent extremity of either *c* or *d*, and the pinch-cock is removed. The glass stop-cock of the absorption tube is turned gradually so that the fluid in the tube passes slowly into the flask, and, when empty, the tube *f* is again closed by means of the pinch-cock, and the calcium chloride tube disconnected.

The ends of the T tube *e* are loosely introduced into tubes *f* and *g*, and the pinch-cock securing tube *j* opened to a certain extent, so that the T tube and the ends of the rubber tubes become filled with water, to the exclusion of air. To this end the internal diameter of the T tube should not exceed 3 mm. The pinch-cock is removed from tube *j*, and the pinch-cocks closing tubes *f* and *g* are alternately opened and closed, and the stopper turned so that a stream of water is directed against different parts of the bulb of the absorption tube. With some practice 75 cc. water will wash every trace of the barium solution into the flask.

The tube *i* is closed with the pinch-cock, and the fluid of the other absorption tube is emptied into the flask in the same way. It is not necessary that the barium solution and wash water from both tubes exceed 250 cc. When the second tube is emptied and washed the tube *i* is closed with the pinch-cock, the absorption tube disconnected, and the barium solution in the flask is titrated with the oxalic acid solution in the burette.

That the processes of filling, emptying and washing these tubes are carried on without the introduction of air containing carbonic acid was proved by omitting the passing of air through the tubes, otherwise carrying on the processes as above, and arriving at the same results as by use of the flask as above in standardising the barium hydrate solution. The tubes can be filled with air free of carbon dioxide and charged with the barium solution and the process begun in thirty minutes, and in the same length of time the tubes can be emptied, washed and the titration made.

The following are the data of one estimation of carbonic acid in the air:

47.9 cc. oxalic acid solution equal 100 cc. of the barium hydrate solution.

Process of absorption from 9 A. M. to 11.40 A. M.

Air passed, 8195 cc.

Thermometer reading at end of process, 20° C.

Barometer reading at end of process, 745 mm.

Manometer reading at end of process, 43 mm.

Vapor tension at 20° C., 17 mm.

$$\underset{\text{Man.}}{43\text{ mm.}} + \underset{\text{V. tension.}}{17\text{ mm.}} = 60\text{ mm.}$$

$$\underset{\text{Bar.}}{745\text{ mm.}} - 60\text{ mm.} = 685\text{ mm.}$$

Volume of air at normal pressure (760 mm.) and normal temperature (0° C.) $= \frac{273}{293} . 8195 . \frac{685}{760} = 6882$ cc.

In titrating, 44.29 cc. oxalic acid solution were required to neutralise the barium hydrate solution; consequently, with the barium solution the equivalent of 3.61 cc. of the oxalic acid solution is combined with the carbonic acid.

As 1 cc. of the oxalic acid solution corresponds to 0.5084 cc. CO_2 at normal temperature and pressure, there is carbonic acid found, $0.5084 \times 3.61 = 1.835324$ cc., therefore in 10,000 vols. air there are $6882 : 1.835324 :: 10{,}000 : 2.66$ vols.

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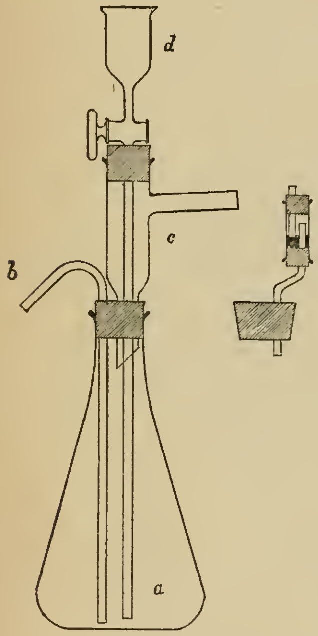
Contributions from the Agricultural Experiment Station of the University of Wisconsin.

APPARATUS FOR KJELDAHL'S METHOD OF NITROGEN DETERMINATION.

By H. P. Armsby and F. G. Short.

One of the chief advantages of Kjeldahl's method for determining nitrogen is found in the fact that a number of determinations may be made simultaneously. So far as the oxidation is concerned, it is a comparatively simple matter to carry on any desired number at once, since they require hardly any attention, but to carry on the subsequent distillation at an equally rapid pace with the common forms of apparatus requires a considerable expenditure of time.

We have therefore endeavored to devise a form of apparatus which should require as little attention as possible during its operation, and should allow us to conduct several distillations at the same time. The apparatus has proved so satisfactory in its operations that we are induced to describe it.



A flask *a*, of any desired form, and of a capacity of about a litre, is closed by a large rubber stopper which carries three tubes. Of these, *b* reaches as nearly as possible to the bottom of the flask, and serves to empty it after the distillation is completed. This is most conveniently done by connecting it with a Richards jet pump. The tube *c* is the exit tube. Where it passes through the stopper it has an interior diameter of about 12 mm., and widens above to about 25 mm. At one side, near the top, is attached an exit tube of such size as to be readily connected with a block-tin condenser. This tube inclines slightly upward. The tube *c* is open at the top, the opening being closed by a rubber stopper carrying a funnel tube *d*, whose stem extends nearly to the bottom of the flask *a*. The annular space about the stem of the funnel tube is filled with glass beads, to arrest any particles of alkali which may be carried over mechanically. The exit tube of *c* is connected with a block-tin condenser the copper jacket of which is 38 cm. long and 5 cm. in diameter and stands at an angle of about 20° with the vertical. To the lower end of the condenser is attached a glass tube dipping into the standard acid contained in a suitable vessel. In our apparatus six flasks and condensers are placed side by side. The condensers are firmly fastened to a light wooden frame, and the water enters at one side and passes through all the condensers successively. The flasks stand upon wire gauze stretched upon two horizontal iron rods about 12 cm. apart, and are sufficiently steadied above by the connection with the condenser. Under each flask is a Bunsen burner, connected by means of a gas-cock with the pipe which supplies the whole. The apparatus is placed upon a small table mounted on casters, and, by simply disconnecting the water and gas, can be wheeled to one side when not in use.

The operation of the apparatus is obvious from the figure. The flask *a* is filled through the funnel tube *d*, the ammonia is evolved through the tube *c*, *b* being closed by means of a pinch-cock, and at the close of the operation the flask is emptied through *b*, as already explained. Water is then poured in through *d* and evacuated through *b*, and the flask is ready for the next distillation.

In order to prevent regurgitation of the standard acid, the stopper of the flask *a* carries, in addition to the two tubes just described, a small mercury trap, as shown in the small figure at the right. The action of this is sufficiently obvious without description. With us it has never failed to prevent any dangerous regurgitation, even with very irregular distillation.

In order to test the apparatus, eleven determinations of nitrogen were made upon a sample of pure ammonium chloride, with the following results:

Nitrogen in Pure NH_4Cl.

1	25.85 per cent.
2	26.21
3	26.52
4	26.39
5	26.53
6	25.78
7	25.84
8	26.31
9	26.17
10	26.34
11	26.31
Average	26.21 ± 0.05 per cent.
Calculated	26.24 per cent.

The probable error of a single determination is ± 0.18 per cent.

of the substance analysed, or ± 0.69 per cent. of the total amount of nitrogen determined.

For the purpose of estimating the error involved in the combined processes of oxidation and distillation, eleven determinations of the nitrogen in a sample of wheat bran were made, with the following results:

Nitrogen in Wheat Bran.

1	2.54 per cent.
2	2.52
3	2.52
4	2.45
5	2.48
6	2.47
7	2.40
8	2.45
9	2.47
10	2.52
11	2.46
Average	2.48 ± 0.008 per cent.
" of 12 determinations by soda lime	2.43 ± 0.015

The probable error of a single determination is ± 0.028 per cent. of the substance analysed, or ± 1.13 per cent. of the total amount of nitrogen determined.

For the determinations of nitrogen in ammonium chloride about 0.12—0.14 gram was usually weighed out; for those in wheat bran 0.5 gram was uniformly taken. The ammonia was received in titrated hydrochloric acid and the excess of acid determined by titrated ammonia, with cochineal tincture as indicator. The fluids had been recently prepared, and the strength of the acid determined by means of pure sodium carbonate; 1 cc. of it was equivalent to .00497 gram of nitrogen. Acid and alkali were measured in calibrated burettes reading to $\frac{1}{20}$ cc. and permitting the estimation of $\frac{1}{100}$ cc.

In addition to the above test-analyses, the apparatus has been used for the regular work of the station for some months. Over 300 determinations have been made by its aid on samples of fodders, milk and fertilizers, and with uniformly satisfactory results, both as regards the apparatus and the method.

Communications from the Chemical Laboratory of Wesleyan University.

II.—ON THE LOSS OF NITROGEN BY PLANTS DURING GERMINATION AND GROWTH.

By W. O. Atwater and E. W. Rockwood.

The apparent escape of nitrogen in several experiments by one of us on the acquisition of atmospheric nitrogen by plants,[1] rendered a study of the question of the liberation of nitrogen from its compounds in germinating seeds desirable. A beginning was attempted in the following experiments.

The question proposed was this: In the germination of seeds and early growth of plants—in this case, peas—may there be any such loss of nitrogen as to materially affect the results of such experiments as those just referred to?

The plan of the experiments consisted in causing peas to germinate under appropriate conditions and cultivating the germinated plants for a longer or shorter time in water or sand. The nitrogen in the seed at the outset was estimated by determining the nitrogen in other peas of the same lot, assuming those experimented with to have the same percentage of nitrogen, weighing the peas used for seed, and computing the nitrogen in them. The nitrogen in the germinated seeds or young plants was determined directly. In the cases in which the plants grew in sand the quantity of nitrogen left behind in the sand at the end of the experiment was determined also. The nitrogen was determined by soda-lime and by Kjeldahl's method, the results by the two methods agreeing closely. The difference between the amounts of nitrogen at the beginning and the end of the experiment showed the loss during germination and growth.

The time of the experiments varied from six to fifty-two days, reckoning from the day when the seeds were first moistened and set to germinating to that when the growth was stopped and the plants taken for analysis. The plants as analysed were thus in various stages of development, from that in which germination was hardly completed to that in which the plants were well on in growth, if the latter expression may be applied to plants which had no food except that contained in the seed and acquired from the air.

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[1] This Journal **6**, 365.

Three series of experiments were made. In those of the first series, which were intended as preliminary tests, the plants had their roots immersed in water. In the second and third series they grew in sand which was kept moistened with water. The water in each case was freed from nitrogen compounds by distilling in the ordinary way, and then redistilling with potassium hydroxide and permanganate, and rejecting so much of the second distillate as gave any visible reaction for ammonia with Nessler's reagent. The remainder of the distillate was regarded as free from nitrogen compounds, and was used for the experiments. The sand was freed from nitrogen compounds by washing and ignition. Portions tested with soda-lime gave no traces of ammonia.

First Series.—Water Culture, in Open Air.

This series included three experiments—Nos. 1, 2 and 3. The peas were germinated in moist paper, and then suspended with the radicles immersed in water as is commonly done in water culture. They were placed in the open window of a room adjoining the main room of our chemical laboratory. The plants were thus protected from rain and dew while exposed to the air. Though the doors connecting with the laboratory were kept closed, some ammonia compounds from the laboratory may very probably have found their way around, through the air outside, to the young plants. The error thus introduced would, of course, decrease the apparent loss of nitrogen. The very minute quantities of nitrogen left behind in the nutritive solutions in the experiments of the succeeding series make it extremely improbable that any considerable quantity of nitrogenous compounds in these experiments could have passed from the seeds or plants into the solutions. At the end of the experiment, when growth was stopped and the plants were taken for analyses, those of Experiment No. 1 were 2—6 cm.; those of No. 2, 3—5 cm.; and those of No. 3, 2—6 cm. in height. The results are stated herewith.

TABLE I.

Experiments in Water Culture, in Open Air.

Exp't No.	Number of Peas.	Time of Germination and Growth.	Nitrogen.			
			In Seeds at beginning of Experiment.	In Plants at end of Experiment.	Lost during Germination and Growth.	
					Total.	Per Cent.[1]
		days.	mgm.	mgm.	mgm.	
1	23	8	215.6	197.5	18.1	8.4
2	8	10	67.5	60.9	6.6	9.8
3	5	15	41.4	40.8	0.6	1.5

The fact that the plants fifteen days after germination showed so little loss of nitrogen, only 1.5 per cent. of the total nitrogen of the seeds, may very likely have been due to absorption of ammonia from the air by the water and the foliage. The results of this and of the other experiments, as well as *a priori* considerations, would lead to the supposition that no definite and regular relation exists between the time of duration of the experiment and the amount of nitrogen lost. That the absorption of ammonia, which would be expected in an atmosphere containing ammonia salts, does actually take place to a large extent even so early in the period of growth, was shown by two experiments, Nos. 4 and 5, which were made in the same manner as Nos. 1, 2 and 3, except that the plants stood inside the window of one of the working rooms of the laboratory. At the time of the experiments the laboratory was used but little, and much less ammonia was afloat in the air than usual. The window was closed most of the time. At the end of the experiment the plants were from 1 to 6 cm. high. Nessler's reagent gave visible traces of ammonia in the water. The results are annexed.

TABLE II.

Plants in Air of Laboratory. Water Culture.

Exp't. No.	Number of Peas.	Time of Germination and Growth.	Nitrogen.			
			In Seeds at beginning of Experiment.	In Plants at end of Experiment.	Gain.	
					Total.	Per Cent.
		days.	mgm.	mgm.	mgm.	
4	29	9	290.2	309.4	19.2	6.6
5	12	9	119.7	129.9	10.2	8.5

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[1] Of amount in seeds at beginning.

It is possible that part of the loss of nitrogen observed in Nos. 1, 2 and 3 may have been due to solution of nitrogenous matter by the water in which the roots were immersed. Though this source of error, as already stated, was in all probability extremely small, an attempt to avoid it was made in experiments in sand culture, in which the nitrogen left in the water about the roots was also determined.

SECOND, THIRD AND FOURTH SERIES.—SAND CULTURE, IN OPEN AIR AND IN GREENHOUSE, ETC.

The peas of these series were either germinated in sand, in which they were allowed to remain a longer or shorter time for subsequent growth, or first germinated in a Nobbe's apparatus and then transferred to sand. The sand was contained in either small beakers or porcelain evaporating dishes, and kept reasonably moist during the experiment.

Second Series, Nos. 6, 7 and 8.—The peas, 12 in number, of each experiment were planted in sand in a small beaker. The sand was from 3 to 4 cm. deep, though the peas were covered to less depth. The beakers were kept in the open air, but protected from rain and dew. At the end of the experiment the beakers with their contents were heated in a drying oven to stop the growth. Within a day or two the sand was separated as accurately as convenient, both sand and plants were dried, and the nitrogen was determined in each. Results are given in Table III beyond. Here follow some of the details.

No. 6.—Time, 6 days. Radicles 1—4 cm. long. But one plumule had appeared above the sand, though the growth seemed to be normal.

No. 7.—Time, 10 days. Radicles 2—5 cm. long. One plumule in sight above the sand.

No. 8.—Time, 14 days. Radicles 2—5 cm. long. One plumule above the sand. One pea had not sprouted. A crust, which seemed to contain organic matter, had formed on the top of the sand. Decided indications of decay were apparent. The experiment appears, therefore, to have been abnormal.

Third Series, Nos. 9, 10 and 11.—The peas in each case were germinated in a germinating apparatus, and then transferred to a porcelain capsule, covered with sand and placed in a greenhouse.

No. 9.—Time, 4 days in germinating apparatus and 14 in sand; total, 18 days. Radicles 1—2 cm. long when taken from apparatus. Plants at end of experiment about 3 cm. high.

No. 10.—Time, 6 days in germinating apparatus and 22 in sand; total, 28 days. Radicles 1—2 cm. long when taken from apparatus. Vines 2—5 cm. high at end of experiment.

No. 11.—Time, as No. 10, except that the plants remained 46 days in the sand, making the whole period 52 days. The plants were from 13 to 15 cm. high, but had not seemed to grow much during the last two weeks, and the leaves had begun to turn yellow. Tendrils had appeared.

Fourth Series, Nos. 12 and 13.—Method as in previous series, but experiments made some weeks later and in a dwelling-house.

No. 12.—Total time, 29 days. Vines 2—7 cm. high. The peas with the smallest vines showed signs of decay.

No. 13.—Time, 42 days. Vines 6—10 cm. high, had not grown for some time. Leaves had begun to turn yellow, as was the case in No. 11.

In both 12 and 13 the sand was washed from the roots with water, and the washings dried with the sand for nitrogen determination. Oxalic acid was added to the washings to prevent loss of ammonia.

In several of the above cases portions of the sand were treated with water, and the extract concentrated and tested for nitrates with ferrous sulphate and sulphuric acid. In No. 8, in which one of the peas failed to sprout, there was a faint trace; in the others none were found. Besides the plainly visible marks of decay in No. 8, there were less decided indications of decay in some of the others.

In the experiments in sand culture very minute quantities of nitrogen were left in the sand. Part of this, in the second and third series at least, came from the minute fragments of the roots, which were not easily separated from the sand. The inference is, that only extremely small quantities of soluble nitrogenous compounds could have been extracted from the roots by the water which surrounded them. It seems fair to infer, as above stated, that but little of the loss observed in the first series could have been due to this cause.

TABLE III.

Experiments in Sand Culture.—Second Series, in Open Air; Third, in Greenhouse; Fourth, in a Room of a Dwelling-House.

Series.	Exp't No.	Number of Peas.	Time of Germination and Growth.	Nitrogen.					
				At beginning of Exp't. In Seed.	At end of Experiment.			Loss during Germination and Growth.	
					In Plants.	In Sand.	Total.		
			days.	mgm.	mgm.	mgm.	mgm.	mgm.	per cent.
2d	6	12	6	100.3	91.7	2.6	94.3	6.0	5.9
	7	12	10	102.9	89.2	2.8	92.0	10.9	10.6
	8	12	14	109.7	81.5	11.6[1]	93.1	16.6	15.1
3d	9	12	18	115.6	100.3	6.9[1]	107.2	8.4	7.3
	10	12	28	103.4	83.2	7.5[1]	90.7	12.7	12.4
	11	12	52	101.4	80.9	4.0[1]	84.9	16.5	16.3
4th	12	10	29	88.3	81.1	...	81.1	7.2	8.2
	13	10	42	88.2	75.6	2.9	78.5	9.7	11.0

It seems, then, that in each of these experiments nitrogen was liberated; that the loss in each series commenced during germination; that there was an apparent recovery in the experiments in water culture, due most probably to acquisition of nitrogen from the air in the form of ammonia or otherwise, but that in the experiments of the last three series the escape of nitrogen continued until the end. The probable causes of this loss demand at least a brief consideration.

THE LIBERATION OF NITROGEN IN GERMINATION AND GROWTH, BY DECAY AND OTHERWISE.

It has been urged—*e. g.*, by Duclaux[2] and Jorisson[3]—that the formation of diastase in germination depends upon the action of microbes. The loss of nitrogen from germinating seeds, and the fact that forms of fermentation which are clearly due to microbes are likewise accompanied by escape of nitrogen from its compounds, would, at first thought, seem to favor the belief that microbes are essential to germination. But the lately published observations of Laurent[4] imply that normal germination takes place independently of micro-organisms. The latter observer finds that the reduction of nitrates to nitrites in presence of germinating seeds, which others have attributed to microbes, is likewise caused by the seed itself in germinating in absence of microbes.

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[1] The sand contained considerable quantities of fragments of roots, etc.

[2] Compt. Rend. **100**, 67; See also observations of Pasteur, *loc. cit.* 68.

[3] Ber. **18**, II, 79.

[4] *Ibid.* **19**, II, 33.

The decomposition of nitrogenous organic compounds and of nitrates in the presence of organic matter, with escape of nitrogen in the free state or in its lower oxides, is a fact well established, but not yet completely understood.[1]

Schlösing has shown[2] that nitrates may be decomposed in soil with evolution of free nitrogen. This appeared in Schlösing's experiments to be dependent upon the oxidation of organic matter at the cost of the oxygen of the nitrates.

Still later observations by Gayon and Dupetit,[3] and by Dehérain and Maquenne,[4] confirm the very large reduction of nitrates in presence of decomposing organic matter, and indicate that this denitrification is due to ferments, as has also been pointed out by Springer.[5] It appears that the presence of organic matter and the absence of oxygen are requisite to the action of these denitrifying ferments, and that not only free nitrogen, but its lower oxides and ammonia, are evolved.

At the beginning of his well-known studies upon the sources of the nitrogen of plants,[6] Boussingault tested the loss of nitrogen in the germination of clover and wheat. Seeds of clover germinated in air on a porcelain plate showed no considerable gain or loss of nitrogen up to the time when the leaves began to appear. Similar results were obtained with wheat, in which the experiment was continued until the green parts predominated in the seed and the stems were 3—5 centimeters long. Boussingault concluded that "clover and wheat in germinating neither gained nor lost nitrogen."

In experiments preliminary to their likewise well-known researches "On the Sources of the Nitrogen of Vegetation,"[7] Messrs. Lawes, Gilbert and Pugh made several series of experiments on the question of the escape of nitrogen from nitrogenous organic matter. In one series, wheat, barley and bean meal were mixed with ignited pumice and with ignited soil, put in a bottle through which washed air was passed, moistened, and kept from June 10 to October 8. In one case there was no loss of nitrogen, in five

[1] See Reiset, Compt. Rend. **42**, 53; Ville, *loc. cit.* **43**, 143; König and Kiesow, Landw. Jahrb. 1873, 107; Armsby, Am. Jour. Sci. [3], **8**, 337; Dietzell, Centbt. f. Ag. Chem. 1882, 417; Reder, *loc. cit.* 1884, 652; Morgen, Landw. Vs. St. **30**, 199 and 429; Kellner, *loc. cit.* **32**, 57; and others quoted beyond.

[2] Compt. Rend. **77**, 202 and 353.

[3] Compt. Rend. **95**, 944.

[4] *Loc. cit.* **95**, 691, 634.

[5] This Journal **4**, 452; Proc. Am. Asso. **18**, 172.

[6] Ann. Chim. Phys. [2], **67**, 5.

[7] Phil. Trans. 1861, II, 499.

others from 3 to 13 per cent. of the nitrogen escaped, apparently as free nitrogen. In another series, seeds of wheat, barley and beans were kept under similar conditions from March 16 until August 18. The seeds germinated and the plants grew for a time, but finally decomposed. From none to 40 per cent. of the nitrogen escaped, one-eighth to one-half of the liberated nitrogen passing off in the form of ammonia. The authors were unable to trace any connection between the different conditions of the experiments and the quantities of nitrogen given off.

To learn to what extent nitrogen would be liberated from seeds or plants in more nearly normal conditions of growth, the same experimenters conducted a series of trials in which wheat, barley and beans were put in ignited pumice and ignited soil in pots and kept in confined air under a large glass shade 16 inches in diameter, on a table, in the diffused light of the laboratory. The plants were at first supplied with distilled water, but with no carbonic acid beyond that which might be contained in the water. The seeds were put in May 1st; the plants grew "tall, slender, delicate," until June 10th, when growth had ceased. Analysis showed no considerable difference between the quantities of nitrogen in the plants and in the seed. The authors conclude that their experiments "in regard to the question of assimilation will not be affected by a loss of free nitrogen, as the result of decomposition of nitrogenous organic matter, as long as that matter is subjected to the ordinary process of germination and exhaustion to supply materials for growth."

The specific question of the loss of nitrogen during the germination and subsequent growth of plants has been studied by several other investigators. Hellriegel caused seeds of winter rape (*Brassica nap. oleif.*) to germinate in confined air under glass. At the end of the period of germination, which, as it would appear from his description, he regarded as terminating when the cotyledons had turned green, no escape of nitrogen was detected by analysis.[1]

Schulz, in an extended series of trials,[2] in which seeds of Leguminosae and Cruciferae, lupine beans, pepper grass, etc., were germinated in presence of pure water in closed vessels, and the resulting gaseous mixtures analysed, found considerable quantities of nitrogen to be set free. He concludes that in the first *stadium* of germination, by which he designates the period which precedes the

[1] Jour. prac. Chem. **64**, 1855, 100 and 107.

[2] *Loc. cit.* **87**, 1862, 129.

bursting of the seed-coat and the appearance of the radicle, there is, along with the purely endosmotic absorption of water and oxygen, a decomposition of albuminoid compounds with formation of carbonic acid and liberation of nitrogen, while hydrogen is set free later.

In the second *stadium*, by which he understands the time from the first visible formation of new cells to the formation of the first leaves, nitrogen, hydrogen and carbonic acid are evolved. The quantities of nitrogen liberated in his experiments were, in some cases, very considerable. Schulz very pertinently calls attention to the difference between the normal changes of germination and those of decay (*Fäulniss*), or *putréfaction*, as it was designated by Saussure, who, like Rolle, Ingenhousz, Sennebier and Davy, had previously studied the same subject. In experiments with seeds which had been crushed so as to prevent germination, and thereafter subjected to the same conditions as the seeds which germinated, nitrogen and carbonic acid were found in each case, but hydrogen in no case, in the gaseous mixture given off. That is to say, in the case of the germinating seeds, the liberation of nitrogen and hydrogen and carbonic acid accompanied germination, while in the putrefaction of the crushed seeds which could not germinate, carbonic acid and nitrogen were liberated without hydrogen. Schulz also very aptly insists on the differences between plants of different species in respect to the chemical changes in germination.

Day[1] has made experiments on the germination of barley, a collateral object being to ascertain whether atmospheric nitrogen takes any active part in the germination. The seeds were kept in confined air over mercury. He cites Mülder as saying that in germination a small quantity of nitrogen gas is absorbed, but finds in his own experiments that the total quantity of nitrogen in the confined volume of air in which the germinating barley was placed was sometimes increased and sometimes diminished to a very small extent, and infers that nitrogen takes no active part in the germination. He does not consider the liberation of nitrogen at all, but his results evidently show that no great quantity was lost.

In the experiments referred to at the beginning of this article as made by growing peas in sand with nutritive solutions, and which led to our experiments here detailed, the seeds germinated and the plants grew in the presence of the nitrates of the nutritive solutions. Boussingault[1] has reported a loss of nitrogen when seeds were germinated in presence of nitrates, which loss he refers to the nitrates rather than to the seeds. Ten beans, weighing 10.533 grams, were allowed to germinate in a barren soil to which 0.3 gram of potassium nitrate was added, the germination taking place in the dark. At the end of 21 days, nearly half (45.3 per cent.) of the nitrogen of the nitrate had disappeared, while neither plants nor soil contained any nitrogen compound into which the nitrogen lost from the nitrate could have been changed. The natural inference was that the nitrogen must have escaped in the form of gas. In an experiment with maize a still greater loss of nitrogen was observed. The development of the plants was, in Boussingault's opinion, too vigorous to admit the supposition that *débris* from the plants could have furnished organic matter to reduce the nitrates, and he was led to the supposition, afterwards strengthened by experiments made at his instigation, that the nitrates were reduced by organic matter excreted by the roots of the plants. This explanation was, however, suggested before the observations of Gayon and Dupetit, and others above mentioned, which indicate that the reduction of nitrates in presence of organic matter may be brought about by micro-organisms.

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[1] Jour. Chem. Soc. 1880, Trans. 646.

In his studies on nitrification by bacteria,[2] Warington calls attention to the "curious fact that when fresh soil [containing the nitrifying ferments] is added to . . . . solutions suitable for nitrification, a destruction of nitrates already present precedes the commencement of nitrification." This disappearance of the nitrates he refers to the reducing bacterium observed by Dehérain and Maquenne and others, and which are active in absence of oxygen.

Frankland and Jordan have studied the action of "hay bacilli," "the micro-organisms which convert grass into hay or ensilage," and which "exist in vast numbers in grass. In the presence of free oxygen they absorb this gas and evolve carbonic anhydride and nitrogen, and these are the gaseous products in the making of hay. . . . . The absorption of oxygen is not necessary, for carbonic anhydride is evolved in an atmosphere of hydrogen; but under these circumstances very little nitrogen makes its appearance. The fermentation goes on under water, but its character is changed. The gases, which are much augmented in volume, now consist of carbonic anhydride (84.63 per cent.), hydrogen (6.9 per cent.), nitrogen (5.83 per cent.), and traces of other combustible gases. Acetic acid, lactic acid, and probably butyric acid, are at the same time formed. This is probably the kind of fermentation by which grass is converted into ensilage."[1] Kellner and others have observed large losses of nitrogen from vegetable matters confined out of access of air, as is done in ensilage. Kellner, however, is not inclined to ascribe the loss of nitrogen to fermentation.[2]

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[1] Ann. Chim. Phys. [5], **22**, 1881, 433.

[2] Jour. Chem. Soc. 1884, Trans. 669.

CONCLUSIONS.—LOSS OF NITROGEN.

The results of the experiments above detailed, and the inferences which, in view of the facts at hand, seem to us warranted, may be thus summarised.

The conditions of the experiments and quantities of nitrogen lost were as in Table IV.

TABLE IV.

Conditions of Germination and Growth of Peas.		Experiments. Series.	No.	Time of Germination and Growth.	Nitrogen Lost, in Per Cent. of Total in Seed at beginning of Experiment.
Water Culture.					
Seeds germinated and then suspended with roots immersed in pure water. Experiments in open air.		1st.	3	8 days.	8.4 per cent.
			1	10 "	9.8 "
			2	15 "	1.5 "
Sand Culture.					
Seeds germinated and grown in sand. Experiments in open air.		2d.	6	6 days.	5.9 per cent.
			7	10 "	10.6 "
			8	14 "	15.1 "
Seeds germinated and then transferred to sand.	Experiments in greenhouse.	3d.	9	18 days.	7.3 per cent.
			10	28 "	12.4 "
			11	52 "	16.3 "
	Experiments in dwelling-house.	4th.	12	29 days.	8.2 per cent.
			13	42 "	11.0 "

In the experiments of the first series, in which the peas were germinated in paper and thereafter kept a short time in open air, with the roots in water, there was in each case a loss of nitrogen. The loss was largest, 9.8 per cent., in the case where growth was stopped at the end of ten days. The failure to find any considerable amount of nitrogen in the water about the seeds in the sand experiments implied that very little nitrogen could have been taken from the seeds by the water. Where the plants were allowed to grow five days longer the loss was only 1.5 per cent. This last result may be explained by acquisition of nitrogen as ammonia or otherwise from the air, the loss being thus nearly made up. It will be remembered that the plants of this series were grown near the chemical laboratory, from which ammonia compounds would naturally escape into the air and thus become available to the plants.

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[1] Jour. Chem. Soc. 1885, Trans. 180.

[2] Landw. Vs. St. **32**, 56, 71.

In the experiments of the second series, in which the seeds were germinated and grown in sand and kept in open air long enough to make the whole duration of the experiment from 6 to 14 days, the loss of nitrogen varied from 5.9 per cent. in 6, to 15.1 per cent. in 14 days. There was, therefore, either larger loss of nitrogen or less acquisition of nitrogen in the longest period than in the experiment in water culture.

In the experiments of the third and fourth series, in which the seeds were germinated in a germinating apparatus during 4—6 days, and were then put in sand and grown in a greenhouse (3d series) or in a dwelling-house (4th series) for longer periods, there was in each case a loss of nitrogen. The loss in each series increased with the duration of the experiment.

In the first two experiments of each of the first two series, the plants had passed but little beyond the period of germination proper. The loss of nitrogen in each of these four cases was from about 5 to 10 per cent. of the whole nitrogen in the seed.

The increased loss of nitrogen with increased duration of the experiments in the last three series indicates that the liberation of nitrogen, which commenced when the seeds were germinating, continued during the whole life of the plants.

In two cases, Nos. 8 and 12, there were very evident indications of decay. That there may have been decay in the other cases seems to us not improbable. The supposition, indeed, seems most reasonable, when we consider how often decay is observed in seeds during and after the period of germination.

The data from other sources above cited show that decomposition of nitrogenous matters, organic and inorganic, is often, but not always, accompanied by liberation of nitrogen; that the decomposition is often, if not always, dependent upon microbes; and that, in many cases at least, the liberation of nitrogen is due to microbes. It is therefore difficult to avoid the inference, although the proof is not absolute, that all three phenomena—action of microbes, decomposition, and liberation of nitrogen—are correlated.

As regards germination, the best evidence at hand seems to us to imply that the agency of microbes is not essential to the normal process. The facts that nitrogen is sometimes, but not always, liberated from germinating seeds, and that the liberation was observed, in our experiments particularly, to continue long after the period of germination had passed, coupled with the well-attested presence of microbes in many cases in which loss of nitrogen has been observed, and their undeniable action in liberating nitrogen, would seem to indicate that both their presence and the liberation of nitrogen are incidental concomitants of germination, and by no means essential to the process. They might thus be regarded as forms of decay, which, like other forms of disease, in higher as well as in lower organisms, either do not appear or are strongly pronounced, according to the circumstances of each case.

The general conclusions which these considerations seem to us to warrant may be still more briefly summarised as follows:

1. The decomposition of nitrogenous organic matter, living and dead, and of nitrates as well, is often attended by evolution of nitrogen in either the free state or in its compounds, or in both. This liberation of nitrogen is sometimes, if not always, due to microbes. It may be large or inappreciable, according to the circumstances of each case.

2. The germination of seeds is sometimes, but not always, accompanied by loss of considerable quantities of nitrogen. The balance of evidence at hand seems to us to decidedly favor the hypothesis that germination without microbes and without the liberation of nitrogen is the normal process.

3. In this view both the action of microbes and the liberation of nitrogen, either in the free state or in the lower oxides or ammonia, which has been attested not only in germinating seeds, but in the later periods of growth of the plant, must be regarded as simply forms of decay. They would thus be not essential to germination and growth, but accessory phenomena like the zymotic diseases that attack higher organisms.

The bearing of these considerations upon experiments on the acquisition of nitrogen by plants will be discussed in a succeeding article.

ANALYTICAL DETAILS.

Nitrogen in Peas.

	Wt. of Peas. grams.	N Found. gram.	Per Cent. of N.	
Peas used in Series I, Nos. 1 and 2.	1.0242	.03699	3.61	3.59 per ct. of N in peas before germination.
	.8789	.03131	3.56	
	Two determinations by another analyst gave		3.62	
			3.57	

	Wt. of Peas. grams.	N Found. gram.	Per Cent. of N.	
Peas used in Series I, No. 3, and subsequent experiments.	1.000	.03808	3.81	Average, 3.77 per ct.
	1.000	.03699	3.70	
	1.000	.03790	3.79	

Water-free Substance of Peas, and Nitrogen in Same.

	Wt. of Peas. grams.	Wt. of Water-free Substance. grams.	Per Cent. of Water-free Substance.	
Used in Series I, No. 3.	.9361	.8391	89.64	Average, 89.68 per cent.
	1.1523	1.0339	89.72	
	3.77 per cent. ÷ 89.68 per cent. = 4.20 per cent. N in water-free substance.			
Used in Series II and III.	.8229	.7287	88.55	Average, 88.48 per cent.
	1.0756	.9508	88.40	
	3.77 per cent. ÷ 88.48 per cent. = 4.26 per cent. N in water-free substance.			
Used in Series IV.	.5364	.4891	91.18	Average, 91.14 per cent.
	.5193	.4731	91.10	
	3.77 per cent. ÷ 91.14 per cent. = 4.14 per cent. N in water-free substance.			

Nitrogen in Plants and Sand After Growth.

FIRST SERIES.

	Wt. of Vines, Roots, etc. gram.	N Found. gram.	Per Cent. of N.	
No. 1.	.3702	.01552	4.19	Average, 4.19 per cent.
	.5500	.02301	4.18	
	1.8810 grams peas before germination		@ 3.59 per ct. = .0675 gram N.	
	1.4540 grams plants after growth		@ 4.19 per ct. = .0609 “	
			Loss = .0066 “	
			= 9.8 per cent.	
No. 2.	.2069	.01002	4.84	Average, 4.84 per cent.
	.2259	.01092	4.84	
	1.1540 grams peas before germination		@ 3.59 per ct. = .0414 gram N.	
	.8428 gram plants after growth		@ 4.84 per ct. = .0408 “	
			Loss = .0006 “	
			= 1.5 per cent.	

No. 3.

.5000	.02039	4.08	Average, 4.09 per cent.
.5000	.02049	4.10	

5.7180 grams peas before germination =
5.1279 grams w.-fr. @ 4.20 per cent. = .2156 gram N.
4.8295 grams plants after growth @ 4.09 " = .1975 "
Loss = .0181 = 8.4 pr. ct.

No. 4.

.5000	.02544	5.09	Average, 5.09 per cent.
.5000	.02544	5.09	

6.0780 grams plants after growth @ 5.09 per cent. =
.3094 gram N in plants.
7.6982 grams peas before germination =
6.9037 grams w.-fr. @ 4.20 per cent. = .2902 gram N.
.3094 gram — .2902 gram = .0192 gram N gained = 6.6 per cent.

No. 5.

.5000	.02419	4.84	Average, 4.80 per cent.
.5000	.02374	4.75	

2.7083 grams plants after growth @ 4.80 per cent. =
.1299 gram N in plants.
3.1791 grams peas before germination =
2.8510 grams w.-fr. @ 4.20 per cent. = .1197 gram N.
.1299 gram — .1197 gram = .0102 gram N gained = 8.5 per cent.

SECOND SERIES.

No. 6.

Wt. of Vines, Roots, etc. gram.	N Found. gram.	Per Cent. of N.	
.5871	.02199	3.74	Average, 3.73 per cent.
.5398	.02010	3.72	

2.4573 grams plants after growth @ 3.73 per cent. =
.0917 gram N in plants.

Wt. of Sand. grams.	N Found. gram.	Per Cent. of N.	
7.2961	.00100	.013	Average, .012 per cent.
6.6435	.00070	.011	

21.1988 grams sand @ .012 per cent. = .0026 gram N in sand.
2.6620 grams peas before germination =
2.3553 grams w.-fr. @ 4.26 per cent. = .1003 gram N.
.1003 gram — (.0917 gram + .0026 gram) =
.0060 gram N lost = 5.9 per cent.

No. 7.

Wt. of Vines, Roots, etc. gram.	N Found. gram.	Per Cent. of N.	
.5182	.01701	3.28	Average, 3.24 per cent.
.4592	.01463	3.19	

2.7523 grams plants after growth @ 3.24 per cent. =
.0892 gram N in plants.

Wt. of Sand. grams.	N Found. gram.	Per Cent. of N.	
6.1931	.00090	.014	Average, .015 per cent.
6.7515	.00109	.016	

18.5573 grams sand @ .015 per cent. = .0028 gram N in sand.
2.7301 grams peas before germination =
2.4156 grams w.-fr. @ 4.26 per cent. = .1029 gram N.
.1029 gram — (.0892 gram + .0028 gram) =
.0109 gram N lost = 10.6 per cent.

No. 8.

Wt. of Vines, Roots, etc. gram.	N Found. gram.	Per Cent. of N.	
.5087	.01851	3.64	Average, 3.62 per cent.
.5240	.01881	3.59	

2.2518 grams plants after growth @ 3.62 per cent. =
.0815 gram N in plants.

Wt. of Sand. grams.	N Found. gram.	Per Cent. of N.	
6.8208	.00418	.061	Average, .060 per cent.
5.8250	.00348	.059	

19.3000 grams sand @ .06 per cent. = .0116 gram N in sand.
2.9103 grams peas before germination =
2.5750 grams w.-fr. @ 4.26 per cent. = .1097 gram N.
.1097 gram — (.0815 gram + .0116 gram) =
.0166 gram N lost = 15.1 per cent.

THIRD SERIES.

No. 9.

Wt. of Vines, Roots, etc. grams.	N Found. gram.	Per Cent. of N.	
.5000	.01620	3.24	Average, 3.28 per cent.
1.0000	.03329	3.33	

3.0585 grams plants after growth @ 3.28 per cent. =
.1003 gram N in plants.

Wt. of Sand. grams.	N Found. gram.	Per Cent. of N.	
6.0115	.00216	.036	Average, .028 per cent.
6.0000	.00118	.020	

24.7210 grams sand @ .028 per cent. = .0069 gram N in sand.
3.0663 grams peas before germination =
2.7130 grams w.-fr. @ 4.26 per cent. = .1156 gram N.
.1156 gram — (.1003 gram + .0069 gram) =
.0084 gram N lost = 7.3 per cent.

No. 10.

Wt. of Vines, Roots, etc. grams.	N Found. gram.	Per Cent. of N.	
1.0000	.0198	1.98	Average, 2.00 per cent.
.5000	.0101	2.02	

4.1576 grams plants after growth @ 2.00 per cent. =
.0832 gram N in plants.

Wt. of Sand. grams.	N Found. gram.	Per Cent. of N.	
8.0000	.00147	.018	Average, .022 per cent.
8.0000	.00206	.026	

34.1620 grams sand @ .022 per cent. = .0075 gram N in sand.
2.7430 grams peas before germination =
2.4270 grams w.-fr. @ 4.26 per cent. = .1034 gram N.
.1034 gram — (.0832 gram + .0075 gram) =
.0127 gram N lost = 12 4 per cent.

No. 11.

Wt. of Vines, Roots, etc. grams.	N Found. gram.	Per Cent. of N.	
1.000	.01584	1.58	Average, 1.55 per cent.
1.000	.01525	1.52	

5.2190 grams plants after growth @ 1.55 per cent. =
.0809 gram N in plants.

No. 11.

Wt. of Sand. grams.	N Found. gram.	Per Cent. of N.	
8.000	.00099	.012	Average, .011 per cent.
8.000	.00069	.009	

35.998 grams sand @ .011 per cent. = .004 gram N in sand.
2.6914 grams peas before germination =
2.3813 grams w.-fr. @ 4.26 per cent. = .1014 gram N.
.1014 gram — (.0809 gram + .0040 gram) =
.0165 gram N lost = 16.3 per cent.

Fourth Series.

No. 12.

Wt. of Vines, Roots, etc. grams.	N Found. gram.	Per Cent. of N.	
1.7675	.0196	1.11	Average, 1.11 per cent.
1.7676	.0195	1.10	

7.3042 grams plants after growth @ 1.11 per cent. =
.0811 gram N in plants.
The sand contained no nitrogen.
2.3407 grams peas before germination =
2.1333 grams w.-fr. @ 4.14 per cent. = .0883 gram N.
.0883 gram — .0811 gram = .0072 gram N lost = 8.2 per cent.

No. 13.

Wt. of Vines, Roots, etc. grams.	N Found. gram.	Per Cent. of N.	
1.4095	.0199	1.41	Average, 1.37 per cent.
1.4095	.0186	1.32	

5.5147 grams plants after growth @ 1.37 per cent. =
.0756 gram N in plants.

Wt. of Sand. grams.	N Found. gram.	Per Cent. of N.	
11.9095	.0007	.006	Average, .005 per cent.
11.9095	.0005	.004	

50.8123 grams sand @ .005 per cent. = .0029 gram N in sand.
2.3378 grams peas before germination =
2.1306 grams w.-fr. @ 4.14 per cent. = .0882 gram N.
.0882 gram — (.0756 gram + .0029 gram) =
.0097 gram N lost = 11.0 per cent.

Contributions from the Sheffield Laboratory of Yale College.

XXIII.—ON NEW ACID PROPIONATES AND BUTYRATES.

By W. G. Mixter.

Acid Barium Propionate, $(C_3H_5O_2)_2Ba.C_3H_6O_2 + 3H_2O$.—Some time ago Mr. F. M. Strong, of this laboratory, attempted to make barium propionate by adding an excess of freshly prepared barium carbonate to dilute propionic acid. The filtered solution was concentrated until crystals of normal barium propionate separated. The mother-liquor, on standing, yielded tabular crystals unlike those of the normal salt, and which were found to have composition given in Analysis I.

Analysis II is of crystals which formed from a solution of barium propionate containing a large excess of propionic acid, which stood some months in a desiccator containing sulphuric acid. Both lots of crystals were dried between blotting paper. The following are Mr. Strong's analyses:

	Calculated for $(C_3H_5O_2)_2Ba.C_3H_6O_2 + 3H_2O$.	I.	II.	
Ba	33.33	32.42	33.42	33.49
C_9	26.27	27.00	25.68	...
H_{22}	5.35	5.86	5.50	...
O_9	35.05	...	...	...
	100.00			

A portion of substance used for Analysis II was heated to 100°, and after five days ceased to lose weight. The loss was 30.97 per cent.; theory requires 31.14 per cent. of $C_3H_6O_2 + 3H_2O$ in $(C_3H_5O_2)_2Ba.C_3H_6O_2 + 3H_2O$. The acid salt gives off water and acid in dry air at ordinary temperatures, and after some months the anhydrous normal salt is left. The acid barium propionate partly liquefies at 64°, and at 100° some solid salt remains in the liquid. It should be stated that mixtures of the normal and acid salt were obtained in some attempts to make the acid salt.

Acid Strontium Propionate, $(C_3H_5O_2)Sr.C_3H_6O + 3\frac{1}{2}H_2O$.—The writer has recently prepared an acid strontium salt by dissolving strontium oxide in dilute propionic acid, adding as much more acid, and boiling down the solution until crystals separated on cooling. The evaporation was continued some days at ordinary temperature. The long, thin crystals were dried between blotting paper and analysed, with the following results:

	Calculated for $(C_3H_5O_2)_2Sr.C_3H_6O_2 + 3\frac{1}{2}H_2O$.	I.	II.
Sr	23.62	23.66	23.55
C_9	29.14	28.59	28.36
H_{23}	6.21	6.48	6.10
$O_{9\frac{1}{2}}$	41.03	...	...
	100.00		

Another preparation of the salt was heated for 24 hours to 100°, when it ceased to lose weight. The loss was 36.45 per cent.; theory requires 36.16 per cent. for a loss of $C_3H_6O_2 + 3\frac{1}{2}H_2O$, and 37.02 per cent. for $C_3H_6O_2 + 4H_2O$. The acid strontium propionate gives off propionic acid on exposure to the air, and after a few hours is coated with a white powder. It partly melts at 67°, and completely liquefies at 75°.

Acid Calcium Propionate, $2[(C_3H_5O_2)_2Ca].C_3H_6O_2 + 5H_2O$.—Acid calcium propionate was obtained in long needles by the evaporation over sulphuric acid of a solution which was prepared by adding a liberal quantity of dilute propionic acid to a saturated solution of calcium propionate. The crystals were dried with filter paper. Analysis I is of the first crop of crystals, and Analysis II is of crystals from the mother-liquor of the first lot.

	Calculated for $2[(C_3H_5O_2)_2Ca].C_3H_6O_2 + 5H_2O$.	I.	II.
C_{15}	33.58	33.34	33.31
H_{36}	6.72	6.72	6.74
Ca_2	14.92	15.03	15.01
O_{15}	44.78	...	...
	100.00		

The salt reacts acid and gives off acid on exposure to air. It does not melt on heating, but softens and chars. At 100° 0.7215 gram lost, in 8 hours, 0.1594 gram, and in 24 hours, 0.1674 gram, and a solution of the residue was acid to litmus paper. Attempts were made to prepare an acid salt by boiling an acid solution of calcium propionate until crystals separated, and also by allowing an acid solution to evaporate in the open air. Neither lot of crystals was acid to test paper, and both contained calcium corresponding to $(C_3H_5O_2)_2Ca + 2H_2O$.

Acid Barium Isobutyrate, $(C_4H_7O_2)_2Ba.C_4H_8O_2$.—Mr. H. E. Andrews, of this laboratory, made acid barium propionate at the time Mr. Strong did, and then undertook the preparation of an acid butyrate. He dissolved 20 grams of barium isobutyrate in a small bulk of water, and added a liberal excess of isobutyric acid. The viscous solution was evaporated on a water bath until it solidified on cooling. The salt was then heated to 100° until its weight was constant. The following is Mr. Andrews' analysis:

	Calculated for $(C_4H_7O_2)_2Ba.C_4H_8O_2$.	Found.
Ba	34.33	34.00
C_{12}	36.08	36.19
H_{22}	5.51	5.80
O_6	24.08	...
	100.00	

Acid barium isobutyrate becomes viscid at 74°.

The barium and strontium salts described are analogous, except in water content, to the acid acetates $(C_2H_3O_2)_2Ba.C_2H_4O_2 + 2H_2O$ and $(C_2H_3O_2)_2Sr.C_2H_4O_2 + 2H_2O$.[1] The propionic acid used in the experiments was made from propionitrile.

XXIV.—ON PARA-FORM-NITR-ANILIDE.

By T. B. Osborn and W. G. Mixter.

Para-form-nitr-anilide was made for the purpose of obtaining, by the action of zinc and ammonia upon it, form-azo and form-azoxy bodies. We failed to get any pure compounds. Reduction with ammonium sulphide also gave negative results. Huebner[2] prepared *o*-form-nitr-anilide melting at 122° from *o*-nitraniline and formic acid. *p*-Form-nitr-anilide does not appear to have been described. We made it by adding formanilide slowly to red, fuming nitric acid, specific gravity 1.53, cooled by a mixture of snow and salt. The temperature of the acid was kept below 10°. The acid solution was poured into cold water, and the precipitated form-nitr-anilide was washed with ice-water, and finally with ether. It was crystallised from absolute alcohol and was analysed, with the following results:

	Calculated for $C_6H_4NO_2NHCOH$.	I.	II.
Carbon,	50.60	49.98	50.04
Hydrogen,	3.62	3.61	3.81
Nitrogen,	16.86	17.18	17.11
Oxygen,.	28.92	...	...
	100.00		

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[1] Villiers, Bulletin de la Société chimique **30**, 176.

[2] Ann. Chem. **209**, 339.

p-Form-nitr-anilide is sparingly soluble in hot water, and separates, on cooling, in brownish-red crystals which melt at 192° to 194°. The crystals from absolute alcohol melted at 187°. When distilled with very dilute sulphuric acid the distillate gave reactions for formic acid. Boiled with potassium hydroxide and cooled, yellow, needle-shaped crystals separated, soluble in hydrochloric acid and melting at 143°, showing that *p*-nitraniline was formed.

XXV.—ON PARA-DIBROM-ORTHO-AZO-ACETANILIDE

By C. H. Matthiessen and W. G. Mixter.

Some time ago one of us (W. G. M.) failed to obtain an azo-body by reducing an ammoniacal solution of *o*-nitracetanilide with zinc. A preliminary experiment with brom-*o*-nitranilide indicated the easy preparation of a new compound. We found, however, great difficulty in obtaining pure products. The material used was made by carefully nitrating *p*-bromanilide, melting-point 165°, and crystallising the product from alcohol. It had the melting-point of *p*-brom-*o*-nitracetanilide, and was found to contain nearly the required amount of bromine and nitrogen. In the first experiment brom-nitranilide, 20 grams, was dissolved in hot alcohol, and concentrated ammonia water and platinised zinc powder were added. The brownish-red precipitate which formed remained several days in contact with the zinc. It was filtered, washed with alcohol, digested with dilute hydrochloric acid, and then thoroughly washed with water and alcohol. The yield was 3.9 grams. An analysis showed the absence of oxygen in the substance, and gave results corresponding fairly well with the empirical formula $C_{13}H_{12}Br_2N_4$. This result indicates that the substance is impure brom-azo-aniline; but the fact that it is insoluble in alcohol and hydrochloric acid does not sustain this view. The small quantity of material prevented further investigation of this product of the long action of zinc on brom-nitranilide.

In another experiment 40 grams of brom-nitranilide were dissolved in not sufficient hot alcohol to hold all in solution when cold. To the hot solution strong ammonia water and a large quantity of platinised zinc were added. The whole was frequently shaken. The action was rapid, and was allowed to continue only half an hour. The precipitate was treated as described in the first experiment. Its weight after drying at 100° was 10 grams. The filtrate did not yield another precipitate on further treatment with zinc, and on evaporation left a sticky residue. The following is the analysis of the dry precipitate:

	Calculated for $\begin{array}{c}C_6H_3BrNNHC_2H_3O.\\ \| \\ C_6H_3BrNNHC_2H_3O.\end{array}$	Found.		
C_{16}	42.29	43.07	...	...
H_{14}	3.09	3.19	...	...
Br_2	35.24	31.21	31.23	31.03
N_4	12.33	12.79	12.56	...
O_2	7.05	...	...	...
	100.00			

The deficiency in bromine is possibly due to the removal of this element by nascent hydrogen with formation of some azo-acetanilide. On the supposition that this latter body was present, attempts were made to separate it by means of hot hydrochloric acid, experience having shown that *p*-azo-acetanilide is readily saponified by the acid.[1] In the first trial a portion of the substance was placed in a large bulk of concentrated hydrochloric acid, and the whole was evaporated nearly to dryness on a water bath. The residue, after washing and drying, was found to contain 32.53 per cent. of bromine. Another portion of the substance was placed in a sealed tube with concentrated hydrochloric acid and heated for four hours to 100°. The larger part of the compound remained unaltered. After washing carefully and drying at 100°, it was analysed, with the following results:

	Calculated for dibromazoacetanilide.	Found.	
C_{16}	42.29	42.23	...
H_{14}	3.09	3.04	...
Br_2	35.24	34.22	...
N_4	12.33	13.13	13.14
O_2	7.05	...	...

p-Dibrom-*o*-azoacetanilide has a light red color, is insoluble in alcohol, chloroform and glacial acetic acid. It melts at 280–282°. It is saponified with difficulty by a boiling solution of potassium hydroxide in alcohol, yielding a dark red, feebly basic body, which is soluble in alcohol. We tried several times to make dibromazoanilide by saponifying the dibrom-azo-acetanilide, and failed to obtain a pure product, or even one free from oxygen.

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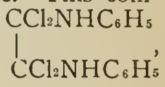
[1] Mixter, this Journal **5**, 284.

XXVI.—ON HALOGEN DERIVATIVES OF OXANILIDE.

By J. O. Dyer and W. G. Mixter.

The action of the halogens on oxanilide has been studied but little. Gerhardt,[1] by treating oxanilide with bromine, obtained a substance soluble in ether, which is not further described, except that it crystallises from the ethereal solution. Wallach,[2] by acting upon oxanilide with phosphorus pentachloride, and treating the product with hydrogen sulphide, got thio-oxanilide. This compound was doubtless formed from oxanilide chloride,



$$\begin{array}{l} CCl_2NHC_6H_5 \\ | \\ CCl_2NHC_6H_5 \end{array},$$

which Wallach did not isolate.

Action of Chlorine on Oxanilide.

In the first attempt to make a chlor-oxanilide, chlorine was passed into a boiling glacial acetic acid solution of oxanilide. There slowly separated what appeared to be small crystalline scales, which the microscope showed to be made of interlaced fibres. The product was filtered, washed with hot glacial acid and alcohol, and dried at 100°. The following is the analysis of the substance, which is designated as preparation *A*.

	Calculated for trichlor-oxanilide.	Found.	
		I.	II.
C_{14}	48.90	48.26	48.58
H_9	2.62	3.03	3.11
Cl_3	31.00	30.88	...
N_2	8.15	8.17	8.26
O_2	9.33	...	...
	100.00		

Too little substance remained for experiments to show whether it was trichlor-oxanilide or a mixture of equal molecules of dichlor-oxanilide and tetrachlor-oxanilide. As the formation of a compound with two atoms of chlorine in one benzene group, and one atom of chlorine in the other benzene group, of oxanilide is of some theoretical interest, we tried, after having found that prolonged action of chlorine forms a higher chlorinated body, the following experiment: Chlorine was passed into a boiling acetic acid solution of oxanilide until some quantity of scales separated. These were filtered from the hot solution. Chlorine produced in the hot filtrate a precipitate much like the first in appearance, only a little more fibrous. The first product weighed 4.3 grams and yielded 29.02 per cent. of chlorine; the second product weighed 3.5 grams and yielded 34.43 per cent. of chlorine. The determinations correspond to 31.3 per cent. of chlorine in a mixture of the two products, and show the possibility of obtaining a mixture which has the composition of trichlor-oxanilide. Hence the results do prove the formation of this body.

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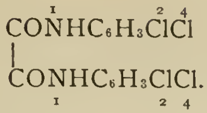
[1] Watts, Dictionary of Chemistry **4**, 286.

[2] Berichte der deutschen chemischen Gesellschaft **12**, 1065; **13**, 527; **14**, 740.

Preparation *B* was made by passing a rapid current of chlorine into a boiling solution of oxanilide in glacial acid. The precipitate, which at first appeared like scales, changed before the stream of chlorine was stopped into a mass of fine white fibres. After the whole mass was cool the product was filtered, washed with alcohol, and dried at 100°. Another preparation, *C*, was made in the same way, only a larger proportion of acetic acid was used, and chlorine was passed into the solution a longer time. The yield of *C* was less than *B*, owing, perhaps, to saponification of the chlor-oxanilide by the long action of the hydrochloric acid in the solution.

	Calculated for tetrachlor-oxanilide.	B.		C.
C_{14}	44.68	46.38	...	46.34
H_8	2.13	2.31	...	2.33
Cl_4	37.23	35.22	35.77	36.36
N_2	7.44	7.75	7.65	7.74
O_2	8.52	...	...	...
	100.00			

The analyses show that the tetrachlor-oxanilide was not free from an oxanilide containing less chlorine. We, however, made from *B* and *C* *m*-dichlor-oxanilic acid, described further on, and *m*-dichlor-aniline, melting at 63°, showing that the tetrachlor-oxanilide made is the meta derivative and has the formula



$$\begin{array}{l} \mathrm{CO\overset{1}{N}HC_6H_3\overset{2}{Cl}\overset{4}{Cl}} \\ | \\ \mathrm{CO\underset{1}{N}HC_6H_3\underset{2}{Cl}\underset{4}{Cl}.} \end{array}$$

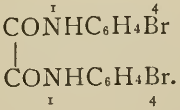
Tetrachlor-oxanilide dissolves readily in boiling aniline, and is but slightly soluble in boiling absolute alcohol, chloroform, benzene and glacial acetic acid. It dissolves in a hot solution of potassium hydroxide in alcohol, and slowly saponifies. Preparation *C* melted at 255°.

Para-dibrom-oxanilide.

When bromine is added in excess to a boiling glacial acetic acid solution of oxanilide, an abundant precipitation of minute crystals of dibrom-oxanilide soon occurs. The boiling should be continued a few minutes to complete the reaction and to get rid of most of the free bromine. After cooling, the precipitate is filtered and washed with alcohol or water. The acetic acid filtrate contains but little of the anilide. The yield is nearly the theoretical quantity. The substance used for the following analysis was dried at 100°:

	Calculated for dibrom-oxanilide.	Found.	
C_8	42.21	41.71	...
H_{10}	2.51	2.62	...
Br_2	40.20	39.03	38.90
N_2	7.04	7.19	...
O_2	8.04	...	...
	100.00		

The substance yielded, when saponified with a boiling concentrated solution of alcoholic potassium hydroxide, *p*-brom-aniline, melting at 63°, and which gave 8.21 per cent. of nitrogen, theory requiring 8.16 per cent. Bromine, therefore, in acting upon oxanilide in solution, as when acting upon other anilides, takes the para position, thus:



$$\begin{array}{l} \mathrm{CO\overset{1}{N}HC_6H_4\overset{4}{Br}} \\ | \\ \mathrm{CO\underset{1}{N}HC_6H_4\underset{4}{Br}.} \end{array}$$

Dibrom-oxanilide dissolves in boiling aniline, and is almost insoluble in boiling absolute alcohol and glacial acetic acid, chloroform and benzene. It melts above 300°.

Para-dijod-oxanilide.

10 grams of oxanilide were dissolved in 300 cc. of boiling glacial acetic acid, and 24 grams of iodine were added. No change was apparent. On adding 25 cc. of nitric acid, sp. gr. 1.40, a violent action commenced and continued some minutes, and a crystalline precipitate resulted. It was filtered at once while hot, and washed with alcohol. Its weight after drying was 14 grams, a yield much less than the theoretical. The alcohol used in washing left, on evaporation, a sticky mass. The acetic acid filtrate gave, when diluted with water, a small precipitate, which was not investigated.

The substance used for analysis was dried at 100°:

	Calculated for dijod-oxanilide.	Found.
C_8	34.15	35.98
H_{10}	2.03	2.09
I_2	51.62	50.06
N_2	5.70	6.01
O	6.50	...
	100.00	

Dijod-oxanilide is saponified by a boiling solution of potassium hydroxide in alcohol, with formation of *p*-jodaniline. The substance analysed was salmon-colored, as was another preparation made by passing chlorine into an acetic acid solution of oxanilide containing iodine. It is white after crystallising from a solution in aniline, in which it dissolves abundantly on boiling. Dijod-oxanilide is but slightly soluble in boiling absolute alcohol, chloroform, glacial acetic acid and benzene. It decomposes at high temperatures before fusing.

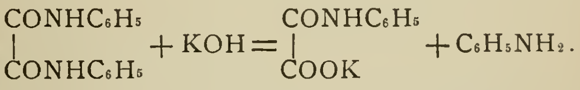
On the Action of Potassium Hydroxide on Oxanilides.

In attempting to saponify, by means of potassium hydroxide, the tetrachlor-oxanilide of preparation *B*, already described, we obtained a potassium salt which was only slightly soluble in cold water. This led to the study of the action of the alkaline hydroxide upon oxanilide and its halogen derivatives.

The first experiment was as follows: 5 grams of stick potash were dissolved in 200 cc. of boiling alcohol, and 5 grams of oxanilide were added. The latter nearly all dissolved at once. Soon small, lustrous crystals appeared. The boiling was stopped after five minutes, and the whole was cooled. The crystalline product was filtered and washed with cold alcohol. The filtrate gave a slight precipitate on addition of barium chloride, indicating the presence of no large proportion of oxalic or oxanilic acid. The crystalline product above mentioned was treated with hot water to separate small quantity of unchanged oxanilide. The potassium oxanilate was changed to the less soluble barium salt by adding to the solution barium chloride. A curdy precipitate formed. The whole was heated to boiling to dissolve the barium salt other than oxalate. The clear solution deposited, on cooling, crystals of barium oxanilate, as shown by the following:

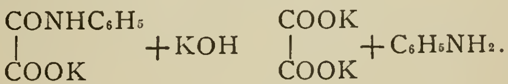
	Calculated for barium oxanilate.	Found.
Barium,	29.46	29.27
Nitrogen,	6.02	5.89

Longer boiling, or a more concentrated solution of potassium hydroxide, completely converts oxanilide into aniline. The reaction, therefore, between oxanilide and the alkaline hydroxide takes place in two stages. First, potassium oxanilate and aniline are formed, thus:



$$\begin{array}{l}CONHC_6H_5\\ |\\ CONHC_6H_5\end{array} + KOH = \begin{array}{l}CONHC_6H_5\\ |\\ COOK\end{array} + C_6H_5NH_2.$$

The potassium salt is next changed by the potassium hydroxide into potassium oxalate and aniline, as foilows:



$$\begin{array}{l}CONHC_6H_5\\ |\\ COOK\end{array} + KOH \quad \begin{array}{l}COOK\\ |\\ COOK\end{array} + C_6H_5NH_2.$$

The first reaction is analogous to the formation of ammonium oxamate from ammonia and oxamide. We have also found that the halogen derivatives of oxanilide undergo the same changes and yield oxanilic acids.

Meta-dichlor-oxanilic Acid.

Two preparations of this acid were made from tetrachlor-oxanilide, already described. 4 grams of the anilide were treated in 125 cc. of boiling alcohol with 5 grams of stick potash dissolved in water. The solution, after boiling ten minutes, deposited a small quantity of potassium dichlor-oxanilate. More separated on cooling. It was filtered, washed with alcohol, and dissolved in small bulk of hot water. From the solution dichlor-oxanilic acid separated as a fibrous mass on addition of hydrochloric acid. It was filtered, washed with water, and dried at 100°. The product was 0.45 gram. In a second trial 3 grams of tetrachlor-oxanilide, 2 grams of potash and 75 cc. of alcohol were taken, and 1 gram of dichlor-oxanilic acid was obtained. The alcoholic filtrate from the potassium dichlor-oxanilate of the first preparation of the acid was evaporated, the residue was washed with water and dried. It melted at 63°, the melting-point of *m*-dichloraniline, and yielded 9.02 per cent. of nitrogen; dichloraniline has 8.65 per cent. The following is the analysis of the dichlor-oxanilic acid:

	Calculated for $CONHC_6H_3Cl_2COOH$.	Found.
C_8	41.06	41.56
H_5	2.14	2.20
Cl_2	30.28	30.10
N	5.99	5.76
O_3	20.53	...
	100.00	

Dichlor-oxanilic acid separates, on cooling a hot, saturated aqueous solution in fibres. 9.71 grams of a solution saturated at 25° left, after evaporation on a water bath, 0.012 gram of residue; hence the acid is soluble in 808 parts of water at 25°. It is soluble in alcohol and ether. It yields, when heated with potassium hydroxide solution, dichloraniline, melting at 63°. Silver nitrate produces in a warm aqueous solution of dichloroxanilic acid a white, flocculent precipitate, which dissolves on boiling, and separates again on cooling. Barium chloride gives a bulky precipitate, soluble in hot water. The silver and barium salts were not further tested. The potassium salt, already alluded to, crystallises, on cooling a hot aqueous solution in white, hair-like fibres. Potassium found, 14.11 per cent.; calculated, 14.29 per cent. Chlorine found, 25.60 per cent.; calculated, 26.05 per cent. Dichlor-oxanilic acid melts at 122°, and at 130° gives off gas slowly.

Para-brom-oxanilic Acid.

When *p*-dibrom-oxanilide is dissolved in a hot dilute solution of potassium hydroxide in alcohol, crystals of potassium brom-oxanilate soon appear. In one experiment we put 5 grams of dibrom-oxanilide into 200 cc. of boiling alcohol and added a concentrated aqueous solution of 5 grams of stick potash. The anilide dissolved readily, and soon crystals separated. The boiling was kept up five minutes, and then the whole was quickly cooled. The potassium brom-oxanilate was filtered, washed with alcohol, and dissolved in a small quantity of boiling water. The solution, on cooling, deposited the larger portion of the salt. In another experiment 10 grams of dibrom-oxanilide were treated with the quantities of alcohol and potash above mentioned. The boiling was continued five minutes. After cooling, the precipitate was washed with alcohol. The alcoholic filtrate, on boiling again, gave more potassium brom-oxanilate. The first precipitate left, when treated with hot water, much dibromoxanilide, which was added to the filtrate from the second precipitate and converted, by heating, into the potassium salt. The three portions of the salt were united and crystallised from hot water. The yield was 3.26 grams of potassium brom-oxanilate. The mother-liquor, on addition of hydrochloric acid, gave a curdy precipitate of brom-oxanilic acid, which, after washing with cold water and drying at 100°, gave results I. Analysis II was of another preparation of the acid, which was crystallised by cooling a hot aqueous solution.

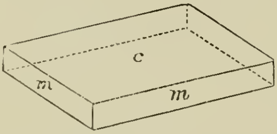
	Calculated for $CONHC_6H_4BrCOOH$.	I.	II.
C_8	39.34	...	39.44
H_6	2.46	...	2.53
Br	32.79	33.09	...
N	5.74	6.08	...
O_3	19.67	...	...
	100.00		

p-Brom-oxanilic acid is soluble in absolute alcohol and ether, and is sparingly soluble in benzene and chloroform. Hot water dissolves it readily, and from the solution, on cooling, crystalline fibres separate. A hot solution was cooled slowly to 25°, and filtered from the crystals which had separated. 9.1047 grams of the solution left, on evaporation on a water bath, 0.0176 gram of brom-oxanilic acid. Hence 1 part of acid is soluble in 515 parts of water at 25°. The solution reacts acid. The acid melts and gives off gases at 198°. It is changed, when heated with potassium hydroxide solution, into *p*-bromaniline.

Brom-oxanilates.

Potassium brom-oxanilate, $CONHC_6H_4BrCOOK$, prepared as already described, gave 13.67 per cent. of potassium, theory requires 13.83 per cent. It crystallises, on cooling a hot aqueous solution in small scales. Mr. S. L. Penfield measured crystals which were obtained from spontaneous evaporation, with the following results.

Crystals are monoclinic, showing simple combinations of prism *m* with base *c*. Habit tabular parallel to *c*. They do not admit of very accurate measurement. The following supplement angles were measured:



$$m \wedge m,\ 110 \wedge 1\bar{1}0 = 97^\circ\ 27'$$

$$c \wedge m,\ 001 \wedge 110 = 83^\circ \quad \text{(about)}.$$

From which the following ratio is calculated:

$$a:b:c = 1.158:1:?;\ \beta = 79^\circ\ 21'.$$

Cleavage very perfect parallel to *c*. Thin tables $\parallel c$ also cleave very readily parallel to their shorter, less readily parallel to their longer diagonal. Plane of the optic axes the clinopinacoid. In the polarising microscope with convergent light one axis can be seen toward the extremity of the field.

Calcium brom-oxanilate, $(CONHC_6H_4Br)_2Ca$, separates as a white curd on mixing solutions of potassium brom-oxanilate and calcium chloride. It is sparingly soluble in hot water and does not crystallise well. The salt taken for analysis was separated by cooling a hot solution. Calcium found, 7.06 per cent.; calculated, 7.07 per cent.

Silver brom-oxanilate, $CONHC_6H_4BrAg$, forms a white precipitate when silver nitrate is added to solution of brom-oxanilic acid or potassium brom-oxanilate. It is soluble, with partial decomposition, in hot water. Silver found, 30.66; calculated, 30.77 per cent.

Barium brom-oxanilate, $(CONHC_6H_4Br)_2Ba$, forms, when barium chloride is added to solution of potassium, brom-oxanilate. It is sparingly soluble in hot water, and separates in small crystals when the solution cools. The barium estimations were of two different preparations of crystals which were dried at 100°. The reason for the deficiency in barium was not determined. Barium found, 21.10 and 21.17 per cents.; theory requires 21.99 per cent.

Para-jod-oxanilic Acid.

p-Dijod-oxanilide, 5.24 grams, was added to 100 cc. of boiling alcohol and an aqueous solution of 5 grams of stick potash was added. The dijod-oxanilide dissolved readily, and soon potassium jod-oxanilate separated. The boiling was continued five minutes, and the whole was cooled. The potassium salt was filtered, washed with alcohol, and dissolved in a small quantity of boiling water. The solution, on cooling, deposited potassium jod-oxanilate in small scales. It was filtered, and after drying at 100°, weighed 1.6 grams. Potassium found, 11.89 per cent.; calculated, 11.92 per cent. To the filtrate from the potassium jod-oxanilate hydrochloric acid was added. The bulky white precipitate of jod-oxanilic acid was washed with water and dried at 100°. It weighed 1.4 grams, and gave the following resuts:

	Calculated for $CONHC_6H_4ICOOH$.	Found.
C_8	33.00	33.26
H_6	2.07	2.24
N	4.81	5.18
I	43.62	42.78
O_3	16.50	...
	100.00	

Jod-oxanilic acid melts, with decomposition, at 197–200°. Hot potassium hydroxide solution converts it into *p*-jodaniline. The acid separates in long fibres when a hot solution cools. In one experiment 1 part of jod-oxanilic acid was found to be soluble in 1385 parts of water at 25°. It is soluble in alcohol and ether. Barium chloride and silver nitrate produce precipitates in hot solutions of jod-oxanilic acid.

THE POST-MORTEM DETECTION OF CHLOROFORM.[1]

By Chas. Luedeking, Ph. D.

In an important trial for murder recently held in St. Louis, the author of this paper made a chemical examination of the viscera of the victim, at the request of the coroner, and obtained very decided reactions for chloroform, notwithstanding the fact that the examination was not undertaken until about twelve days after death. The lungs, usually congested in case of death by chloroform, were selected as best suited for its detection. The great volatility of chloroform would seem *a priori* to preclude the possibility of its detection so long after death, and as at the time there was considerable doubt expressed as to the reliability and accuracy of the experiments, the author determined, once for all, to decide the matter by direct experiment, and so set to rest all doubts.

The literature was first scanned carefully to ascertain whether there were any prior experiments in this direction, but nothing could be found. My direct object was then to determine how long after death chloroform can, with certainty, be detected: as also whether or no any substances are generated by the process of decomposition, which might give similar reactions to chloroform, and thus lead to erroneous conclusions.

The manner of experimenting was simple and direct. Dogs of from 15 to 20 pounds weight were destroyed gradually by the administration of chloroform through the lungs in from 5 to 10 minutes. Then the carcasses were allowed to stand in summer's heat or the temperature of the room for different periods of time, and finally the lungs removed and tested for chloroform by the Ragsky method.[2] In the following the experiments are briefly given.

Experiment I.

Carcass exposed on a dissecting table, during full summer's heat, for six days and ten hours. Decomposition far advanced and an exceedingly offensive odor given off. The lungs were removed, and after having been finely minced and rendered *slightly* alkaline by means of sodium carbonate, were heated over a water bath in a flask through which a current of air was slowly passing. The escaping gases were sent through a Bohemian glass tube, which was heated to bright redness over a space of two inches. The iodised starch paper was five inches distant from this heated portion of the tube, and throughout the experiment remained perfectly cool.

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[1] Presented before the St. Louis Academy of Science, June, 1886.

[2] Erdmann's Jour. **46**, 170.

A very strong bluing of the paper was observed and the nitrate of silver solution was strongly precipitated.

EXPERIMENT II.

Carcass exposed during full summer's heat for ten days. It had then lost all solidity, the hair literally falling off by the slightest abrasion. The lungs were removed and examined as in Experiment I. A very decided reaction for chloroform was obtained.

EXPERIMENT III.

Carcass exposed during full summer's heat for fourteen days. The lungs then removed and examined as in Experiment I. The reaction for chloroform was very decided.

EXPERIMENT IV.

Carcass placed in an ice-chest for three weeks, and then exposed for ten days during full summer's heat. The lungs were then examined as in Experiment I, and a strong reaction for chloroform obtained.

I do not hesitate to say that in winter chloroform could be detected without the slightest difficulty for many months after death.

EXPERIMENT V.

Carcass exposed in a room (70° F., very constant) for three weeks and three days. The lungs were then examined as in Experiment I, and a very decided reaction for chloroform obtained.

EXPERIMENT VI.

Carcass exposed in a room (70° F., very constant) for four weeks. The lungs examined as in Experiment I, and a decided reaction for chloroform obtained.

The question now arises whether there cannot be substances formed by the process of decomposition, which, resembling chloroform in certain chemical reactions, might therefore lead to erroneous conclusions. Dr. Ragsky already partially answered this question experimentally. The author made three experiments to this end, which are herewith briefly given.

EXPERIMENT I.

The lungs of a slaughtered bull exposed during full summer's heat for ten days. Not a trace of reaction of chloroform could be obtained by the Ragsky method.

EXPERIMENT II.

The lungs of a slaughtered bull exposed during full summer's heat for fourteen days. Not a trace of reaction of chloroform could be obtained by the Ragsky method.

EXPERIMENT III.

Carcass of a dog destroyed by coal gas was exposed in a room (70° F., very constant) for three weeks and four days. No chloroform reaction could be obtained by the Ragsky method.

CONCLUSIONS.

1. By the process of decomposition no substances are generated which could vitiate the tests for chloroform by the Ragsky method.

2. Chloroform, when it has caused death by inhalation, can with certainty be detected in the body four weeks after death, and, notwithstanding its volatility, it is certainly retained in the viscera in large amount during this time.

In the case which was the cause of these experiments being undertaken, the victim had been dead at least ten days before the body was discovered, in high state of decomposition. On the strength of the Ragsky and Hofmann tests the author gave it as his sworn opinion that the deceased had chloroform in his viscera, whereupon a charge of murder by chloroform was preferred. Maxwell, the culprit, finally, after the lapse of an entire year, made confession that chloroform had indeed been the cause of death.

It being certain, finally, that chloroform can be detected a long time after death, as evidenced by our experiments, we must next try to understand why this should be so. The following may serve to this end.

R. Dubois[1] finds that the vapor of chloroform penetrates into the interior of the tissues, and becomes substituted for normal water. This is not a phenomenon of desiccation or osmose; a true affinity comes into play, the protoplasm absorbing the vapor of the anaesthetic and expelling a certain quantity of water.

Chancel and Parmentier[2] have proven that chloroform has a very decided affinity for water.

The author allowed to stand open a flask containing water, holding a small quantity of chloroform in solution. After two weeks' time the chloroform reactions could still be obtained without any difficulty.

Add to the above that chloroform is a powerful preservative agent,[3] we have a collection of factors sufficient to enable us to understand the lengthy occlusion of chloroform in the animal body, though others of minor importance might be adduced besides these.

Grehaut and Quinquand,[4] experimenting on dogs, find the amount of chloroform necessary to produce anaesthesia to be at least one gram to every two litres of blood. On the basis of these results, the total quantity of chloroform in the blood of a man of 150 pounds weight would be 2¾ grams approximately, when rendered insensible through its inhalation. The amount necessary to produce death would, under normal conditions, certainly not be less than this. Under the assumption that one-sixth of the entire quantity of blood circulating in the body is at all times passing through the lungs, the quantity of chloroform in the lungs of a man of 150 pounds weight, rendered insensible from its inhalation, would be about one-half gram.

We desire to emphasise by this calculation that there is an abundance of material in the lungs for the detection of chloroform. The liver would undoubtedly also be very suitable for its detection.

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[1] Chem. News, 1886, 311.

[2] C. R. **100**, 27.

[3] Robin and Augendre, C. R. **30**, 52; **31**, 679.

[4] C. R. **97**, 753.

ON THE ACTION OF HEAT UPON ETHYLENE.

By L. M. Norton and A. A. Noyes.

In a number of cases where an organic compound consisting largely of carbon and hydrogen has been decomposed by the action of heat, a certain hydrocarbon called crotonylene, C_4H_6, has been observed among the products. It accompanies ethylene frequently when this gas is formed by the action of heat, and its formation has not been observed in any case where ethylene was absent. Thus it is found in illuminating gas,[1] and although it is present in small quantities, yet upon its presence and that of benzol depends to a great degree the illuminating power of coal gas. It seemed of interest to inquire whether this important hydrocarbon was a primary product of decomposition by heat, or a secondary product formed by the action of heat upon ethylene. As the formation of crotonylene by the action of heat upon ethylene alone had never been observed, we have once more passed a current of ethylene through a red-hot tube and examined the products. This subject was first carefully investigated by Marchand,[2] who obtained from ethylene, at a white heat, carbon and hydrogen; then by Magnus,[3] who obtained, at a red heat, methane, hydrogen, carbon and naphthalene. Berthelot,[4] in several investigations, obtained acetylene, ethane, benzol, styrolene and naphthalene.

The ethylene used in our investigation was prepared by the action of sulphuric acid upon alcohol,[5] was purified and stored in large gas-holders. After drying, it was passed slowly through a piece of hard glass tube 15 mm. in diameter, which was maintained at a low red heat for a distance of 60 cm. The products issuing from this tube passed first through a series of U tubes which were surrounded by a freezing mixture. The uncondensed products passed then through an ammoniacal cuprous chloride solution to absorb hydrocarbons of the acetylene series, and then through bromine to absorb hydrocarbons of the ethylene series, and samples of the unabsorbed gases were finally collected over water at the end of the apparatus.

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[1] Berthelot, Comptes Rendus **82**, 930; Tieftrunk, Jour. f. Gasbeleuchtung, 1877, 509; Helbing, Ann. d. Chem. **172**, 281.

[2] J. prak. Chem. **26**, 478. [3] Pogg. Ann. **90**, 1. [4] Comptes Rendus **50**, 805; **62**, 94. Ann. d. Chim. et Phys. **4**, 16, 144, etc.

[5] Erlenmeyer and Bunte, Ann. d. Chem. **168**, 65.

Carbon was deposited in the decomposition tube. A liquid slowly condensed in the U tubes. At the end of one month 15 cc. had been collected. This liquid was divided into four portions, boiling 75°–130°, 130°–230°, 230°–330°, 330°–430°. The portion boiling 75°–130° gave a large fraction boiling from 80°–100°, which solidified in a freezing mixture and was proved, by its specific gravity and the aniline test, to be benzol. A white crystalline solid was obtained from the portion boiling from 130° to 230° which melted at 79° after sublimation, and was naphthalene. A crystalline substance separated from the portion boiling 230° to 330° which, after sublimation, melted at about 200°, and was probably anthracene. Other aromatic hydrocarbons were present in the liquid, but in quantities too small for identification. Faint traces only of a precipitate were found in the ammoniacal cuprous chloride solution. If hydrocarbons of the acetylene series were formed, they must have been immediately destroyed in the hot tube. About 300 grams of bromides of unsaturated hydrocarbons were obtained. These bromides consisted of a mixture of liquid bromides and a solid bromide. Upon distillation the latter remained in the flask. The liquid bromides consisted largely of ethylene bromide from the absorption of undecomposed ethylene. Fractionation and analysis showed that they also contained methylene bromide from the action of bromine on methane,[1] propylene bromide and butylene bromide from the absorption of propylene and butylene by the bromine.

The solid bromide was purified by crystallisation from alcohol and by sublimation, and the analysis then gave the following result:

	Found.	Calculated for tetrabrombutane or crotonylene tetrabromide.
Br	85.66	85.56

This bromide agrees in all its properties with the crotonylene tetrabromide prepared in this laboratory by passing illuminating gas through bromine, and which melts at 115½°, and is also identical with that obtained from the products formed by the action of heat upon hexane and pentane,[2] and without doubt with that obtained by Henninger[3] from the crotonylene from erythrite, and by Armstrong and Miller[4] from the crotonylene from oil gas, and which possesses the constitution $CH_2Br—CHBr—CHBr—CH_2Br$. The crotonylene formed by the action of heat upon ethylene is therefore divinyl, $CH_2 = CH - CH = CH_2$, and it appears probable that its frequent occurrence is to be explained by the equation $2C_2H_4 = C_4H_6 + H_2$. An analysis by explosion of the gases collected over water at the end of our apparatus showed that they consisted of methane and ethane.[1] The products obtained by us by passing ethylene through a red-hot tube and identified were therefore benzol, naphthalene, anthracene (?), propylene, butylene, divinyl, methane, ethane and carbon. Berthelot[2] is of the opinion that the formation of aromatic derivatives from ethylene under the influence of heat is primarily due to the aggregation of molecules of acetylene, and that acetylene is first formed from the ethylene. Jacobsen[3] believes that all aromatic compounds formed by dry distillation originate in compounds of the acetylene series, but he offers no new evidence to sustain his views. The absence of acetylene from the products which we obtained by the action of heat on ethylene shows that, if these views are correct, the circumstances of our experiment must have favored the formation of aromatic derivatives to an extraordinary degree. We incline rather to the view that benzol is formed directly by the action of heat upon ethylene. Furthermore, Armstrong[4] states that Messrs. Thorp and Dyson have again subjected acetylene to the action of heat, and that they find it exceedingly difficult to obtain even a very small quantity of benzol in this way. We propose to extend our investigation to the higher homologues of ethylene.

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[1] Moore, Report on Granger Water Gas, Phil., 1885, 26.

[2] Norton and Andrews, this Journal **8**, 1.

[3] Bull. Soc. Chem. [2] **19**, 145.

[4] Jour. Chem. Soc., 1886, 74.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY, BOSTON, *June*, 1886.

Contributions from the Chemical Laboratory, U. S. Department of Agriculture.

VIII.—VARIATIONS IN THE CHEMICAL COMPOSITION AND PHYSICAL PROPERTIES OF AMERICAN OATS.

BY CLIFFORD RICHARDSON.

In a previous paper[5] a study of the effect of environment on wheat and corn was presented, showing the effect, to a greater or less degree, upon the grain of these two cereals which season, climate, soil and other conditions exert. Since that time our investigations have been extended to oats, with results which have recently appeared in detail in Bulletin No. 9 of the Division of Chemistry of the Department of Agriculture of the United States. Of the cereals first examined wheat was found to be far more susceptible to its environment than corn, and in the present investigation it appears that oats are in their nature somewhat different from either of these grains in their mode of response to controlling causes.

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[1] Day, this Journal **8**, 165.
[2] *Loc. cit.*
[3] Berichte d. deut. chem. Gesell. **10**, 853.
[4] Jour. Soc. Chem. Ind., 1884, 466.
[5] This Journal **6**, 302–317.

This grain is grown under as varied conditions as any cereal, and in appearance is most variable. They will grow and can be made to pay on almost any soil and in all parts of the country, with the result that in weight per bushel and size of the grain and other physical properties there are found the greatest differences. It was reasonable to suppose that the composition of the grain would vary in the same way. This has, however, proved to be dependent on its environment less than wheat.

One hundred and sixty-six specimens of oats have been collected from all parts of the country, and from their examination the following facts have been learned.

In the North white or yellow, black and white, and black oats are principally grown. In the South varieties of the red rust proof are the prevailing crop. In the North the seed is put in in April or May, and harvested in July or August. In the South it is sown in November to January, and harvested in May or June, the growth being made in the cool part of the year. In certain intermediate localities, where the summers are too dry and hot and the winters too cold, it is difficult to do anything with this grain.

The difference in appearance between the crops of these two sections of the country is marked. The Southern oats are large, light, awned varieties, of reddish-brown color, with inflated husks not nearly filled by the kernel. The Northern grain is smaller, more compact, not often awned, and with the husk in the better samples well filled out.

Notwithstanding these characteristics, we learn from averages of the results that the size and weight of the Southern clean kernel are rather larger than the Northern. Their fluffy husk, however, makes them lighter oats in weight per bushel.

Averages have been calculated for various sections as follows: The Northern States include all north of Maryland and Kentucky, together with Missouri, Montana and Dakota; the Southern, all south of these; and the Pacific slope, Colorado, Nevada, New

Mexico, Washington Territory, Oregon and Utah; the Atlantic slope consists of the States east of the Ohio river and the Gulf; the Western States, of those west of this line, excepting those on the Pacific slope.

Average Physical Properties of Oats.

State.	Number of specimens.	Weight of 100 kernels.	Clean grain.	Hulled grain.	Hulls.	Weight per bushel.
			Per cent.	Per cent.	Per cent.	Lbs.
United States	166	2.507	95.00	69.97	30.03	37.2
Northern States	90	2.290	95.63	70.60	29.30	38.0
Southern States	66	2.028	94.18	69.08	30.92	34.5
Pacific Slope	20	2.737	94.93	69.52	30.48	43.2
Atlantic Slope	58	2.523	95.37	69.69	30.31	37.0
Western States	61	2.339	95.82	72.20	27.80	37.8
Maine	3	2.344	97.38	70.29	29.71	38.6
New Hampshire	3	2.472	93.83	71.54	28.46	38.3
Vermont	4	2.474	94.97	69.52	30.48	39.4
Connecticut	4	2.110	95.78	67.44	32.56	35.6
Rhode Island	1	3.029	97.16	67.27	32.73	32.3
New York	8	2.571	95.32	71.00	29.00	39.8
New Jersey	2	2.371	98.50	72.75	27.25	36.6
Pennsylvania	4	2.686	92.24	68.55	31.45	38.0
Ohio	9	2.256	96.42	71.44	28.56	39.8
Michigan	6	2.767	96.22	72.31	27.69	42.3
Indiana	3	2.188	93.36	72.00	28.00	36.7
Illinois	9	2.350	97.21	72.02	27.98	39.4
Wisconsin	5	2.487	94.81	70.77	29.23	39.0
Minnesota	9	2.416	96.09	71.67	28.33	43.6
Iowa	6	2.245	96.99	71.63	28.37	38.4
Missouri	3	1.867	98.13	69.78	30.22	37.8
Nebraska	3	1.763	97.87	70.10	29.90	33.1
Dakota	5	2.519	92.92	66.20	33.80	43.3
Montana	3	2.410	91.06	70.54	29.46	30.0
Maryland	2	2.244	93.26	71.53	28.47	37.5
Delaware	1	1.976	98.04	69.69	30.41	......
Virginia	3	2.657	94.67	65.23	34.77	39.2
West Virginia	4	2.500	95.94	66.48	33.52	39.2
North Carolina	6	2.496	94.52	70.37	29.63	39.8
South Carolina	8	2.767	95.99	69.52	30.48	38.4
Kentucky	4	2.249	94.88	69.99	30.01	31.7
Tennessee	4	2.089	95.66	65.42	34.58	36.3
Georgia	7	2.609	93.39	68.56	31.44	31.6
Florida	5	2.542	97.79	68.94	31.06	29.0
Alabama	5	2.961	96.47	68.17	31.83	31.7
Mississippi	5	2.751	90.40	70.52	29.48	34.4
Louisiana	3	2.957	94.99	69.90	30.10	36.9
Arkansas	1	2.760	97.08	64.10	35.90	35.2
Colorado	3	2.442	90.16	69.80	30.21	43.3
Texas	8	2.924	96.29	71.56	28.44	36.1
Utah	1	2.560	90.72	61.17	38.83	43.5
Nevada	1	2.019	95.05	66.01	33.99	41.8
New Mexico	1	2.462	97.67	73.21	26.79	41.4
Washington Territory	2	3.602	98.34	76.10	23.90	43.1
Oregon	2	3.279	96.97	66.12	33.88	45.6

Oats having the husk (pallets and at times glumes) are necessarily lighter than wheat in weight per hundred grains. The heaviest is from the Pacific slope, and the South ranks next, owing, as has been said, to its large size. In weight per bushel, however, the fluffy husk of the Southern grain makes it the lowest in the country, while the Pacific slope retains the highest weight per bushel, as also size and weight per 100, showing it to have a plump, well-filled grain.

The average for the country, 37.2 pounds, appears rather high in comparison with the most common legal weight, 32 pounds, but the determinations have been proved correct for the specimens examined, and are not mere estimates. The samples are, too, apparently fair averages, as the figures giving percentages of clean grain in the specimens as received show that no particular pains were taken to prepare them for exhibition before reaching us. The range with this cereal is larger than with any other. The extremes in weight per 100 grains were, for the lightest, from Nebraska, 1.582 grams, and from Oregon, for the heaviest, 3.786 grams. Cleanliness varied from 99.8 per cent. to 70.0 per cent., but of course had nothing to do with locality. The heaviest weight per bushel was found in specimens from Colorado and Dakota, weighing 48.8 and 48.6 pounds. The lightest were from Alabama and from Florida, 24.7 and 26.9 pounds respectively.

In milling oats the relation of kernel to waste is about one-half. Our results show that the relation of kernel to husk averages for the whole country 7 to 3, those from the Western States being a little less husky, and those from the South considerably more so. It is, however, the inflated nature of the husk in the Southern grain and the fact that the glume or outer husk is often adherent that affects the weight per bushel more than the slightly larger proportion.

The extremes found were 79.28 per cent. of kernel in a specimen from Washington Territory, and 55.37 per cent. in one from Dakota. Washington and Oregon sustain their reputation for fine looking grain, while the small proportion of kernel in the Dakota specimen is due entirely to harvesting before it was quite ripened. It is hardly a fair example, other specimens from the Territory reaching over 70.0 per cent. of kernel.

In weight per bushel the warm climate of the South so affects the form of the grain as to lower its average 2.7 pounds. This is hardly as large as would be expected, and leads to the conclusion that the climate has a greater effect than some other characteristics. One of these is yield, which, from an average of 30 bushels in the North, falls to about 10 in the South, and, as has been said, the color and shape of the grain are much changed.

The variations in composition which correspond to those in physical properties have been derived in a similar way by analyses of the same samples separated into kernels and hulls. This separation was primarily undertaken to determine the relation of the two portions of the grain, and the analyses were completed of each part, in order that comparison with wheat and of the kernels among themselves might not be influenced by the presence of the husks.

The averages derived from the analyses are as follows:

Average Composition of American Oats, arranged by States.

State.	Number of analyses.	Water.	Ash.	Oil.	Carb-hydrates.	Fibre.	Albuminoids.	Nitrogen.
United States	179	6.93	2.15	8.14	67.09	1.38	14.31	2.28
Atlantic Slope	64	6.84	2.17	8.22	67.10	1.37	14.30	2.28
Northern States	92	7.07	2.19	8.02	66.88	1.37	14.47	2.32
Western States	54	6.98	2.19	7.91	67.06	1.37	14.49	2.32
Southern States	69	6.79	2.12	8.23	67.22	1.35	14.29	2.28
Northwestern States	8	7.38	2.23	8.54	66.96	1.28	13.61	2.18
Pacific Slope	18	6.71	2.10	8.87	67.78	1.53	13.01	2.08
Maine	3	7.19	1.91	8.55	66.40	1.77	14 18	2.27
New Hampshire	3	7.06	2.30	8.36	65.27	1.32	15.69	2.51
Vermont	4	6.33	2.00	8.06	66.15	1.34	15.62	2.50
Connecticut	4	6.54	2.30	8.06	68.07	1.47	13.56	2.17
Rhode Island	1	7.52	2.02	8.71	68.66	1.01	12.08	1.93
New York	9	7.46	2.14	8.02	66.53	1.44	14.41	2.31
New Jersey	2	7.42	2.29	7.14	66.55	1.29	15.31	2.45
Pennsylvania	4	7.10	2.36	8.00	65.85	1.32	15.37	2.46
Ohio	9	6.76	2.25	8.32	65.39	1.19	16.09	2.57
Michigan	6	7.11	2.35	7.74	67.61	1.19	14.00	2.24
Indiana	3	8.05	1.92	7.82	65.69	1.24	15.28	2.45
Illinois	9	6.19	2.34	7.64	67.69	1.55	14.59	2.34
Wisconsin	5	7.27	2.06	7.45	68.46	1.49	13.27	2.12
Minnesota	9	7.16	2.27	7.91	68.33	1.30	13.03	2.09
Iowa	7	7.01	2.03	8.02	66.72	1.44	14.78	2.37
Missouri	3	7.11	1.91	8.35	65.54	1.51	15.58	2.49
Nebraska	3	7.42	2.16	7.98	66.64	1.51	14.29	2.29
Dakota	5	6.74	2.25	8.16	67.39	1.28	14.28	2.27
Montana	3	8.44	2.20	9.18	66.23	1.29	12.66	2.03
Maryland	2	7.01	2.36	7.91	66.39	1.46	14.87	2.38
Delaware	1	5.94	2.27	7.75	66.09	1.35	16.60	2.66
Virginia	4	6.63	2.43	7.93	66.03	1.49	15.49	2.48
West Virginia	4	6.64	2.29	7.51	64.86	1.46	17.24	2.76
North Carolina	6	6.84	2.06	8.27	68.28	1.63	12.92	2.07
South Carolina	8	7.07	2.09	8.48	68.19	1.00	13.17	2.11
Kentucky	4	7.34	2.10	7.80	65.97	1.74	15.05	2.41
Tennessee	4	6.81	2.22	8.09	67.33	1.42	14.13	2.26
Georgia	8	6.15	2.28	8.54	67.65	1.35	14.13	2.26
Florida	5	6.03	2.08	8.49	67.85	1.37	14.18	2.27
Alabama	5	6.40	1.94	8.42	67.55	1.16	14.53	2.33
Mississippi	5	7.41	1.97	7.86	67.48	1.28	14.00	2.24
Louisiana	3	8.12	2.13	8.09	66.55	1.17	13.94	2.23
Arkansas	2	5.80	1.12	7.92	67.59	1.78	14.79	2.37
Texas	8	7.16	2.04	8.71	67.08	1.21	13.80	2.21
Colorado	4	6.06	2.31	7.80	67.50	1.10	15.23	2.44
Utah	2	6.67	2.39	8.49	68.30	1.72	12.43	1.99
Nevada	1	6.80	2 27	9.72	66.21	1.17	13.83	2.21
New Mexico	2	6.83	2.31	9.66	66.16	1.73	13.31	2.14
Washington Territory	2	6.82	1.67	9.28	69.96	1.51	10.76	1.72
Oregon	2	6.86	2.35	8.38	67.77	1.78	12.86	2.06
California	5	7.08	1.76	9.40	67.90	1.71	12.15	1.94

Average Composition of Hulls of Oats, arranged by States.

State.	Number of analyses.	Water.	Ash.	Undetermined.	Fibre.	Albuminoids.	Nitrogen.
United States	100	5.22	5.59	68.83	17.88	2.48	.40
Atlantic Slope	43	4.73	4.78	70.35	17.50	2.64	.42
Northern States	52	4.89	5.69	68.52	18.42	2.48	.40
Western States	33	4.99	6.39	67.88	18.30	2.44	.39
Southern States	43	5.71	5.40	69.20	17.15	2.54	.41
Northwestern States	17	4.57	6.25	68.80	18.35	2.03	.33
Pacific Slope	2	5.16	5.98	67.87	19.15	1.84	.30
Maine	1	4.00	4.30	65.99	23.36	1.75	.28
New Hampshire	3	4.88	4.62	68.19	19.62	2.69	.43
Vermont	4	4.15	4.19	71.08	18.08	2.50	.40
Connecticut	3	5.98	4.70	67.40	19.35	2.57	.41
Rhode Island	1	5.00	4.50	73.12	15.10	2.28	.36
New York	3	4.73	4.43	71.54	16.44	2.86	.40
New Jersey	1	2.90	6.30	68.46	19.19	3.15	.50
Pennsylvania	3	4.28	4.00	69.92	19.47	2.33	.37
Ohio	6	4.51	6.00	69.05	17.84	2.60	.42
Michigan	4	4.51	5.44	68.36	19.67	2.02	.32
Indiana	1	4.80	5.20	68.17	19.38	2.45	.39
Illinois	6	7.01	6.85	64.90	18.43	2.81	.45
Wisconsin	4	3.71	6.58	70.22	17.48	2.01	.32
Minnesota	4	5.24	6.43	67.28	18.77	2.28	.36
Iowa	2	5.25	6.43	67.04	19.18	2.10	.34
Nebraska	1	4.10	7.80	68.40	17.60	2.10	.34
Missouri	2	4.72	6.23	69.85	16.22	2.98	.48
Dakota	1	5.40	7.70	66.50	18.12	2.28	.36
Montana	2	7.40	6.99	68.04	18.38	2.89	.46
Maryland	2	4.20	5.12	66.24	20.94	3.50	.56
Virginia	3	4.08	4.37	69.77	19.03	2.75	.44
West Virginia	2	4.03	4.60	69.85	19.16	2.36	.38
North Carolina	5	5.02	5.92	70.48	15.78	2.80	.45
South Carolina	5	4.23	5.64	73.47	13.93	2.73	.44
Kentucky	3	10.80	5.00	60.87	20.18	3.15	.50
Tennessee	2	6.88	6.00	66.61	18.24	2.27	.36
Georgia	6	5.53	5.13	69.51	17.28	2.57	.41
Florida	3	4.86	2.19	74.44	15.51	2.28	.36
Alabama	2	9.72	4.98	65.68	17.43	2.19	.35
Mississippi	2	5.30	7.28	67.95	17.19	2.28	.36
Louisiana	2	10.30	4.90	63.38	19.23	2.19	.35
Arkansas	1	6.00	5.14	69.08	16.80	2.98	.48
Texas	5	4.06	7.22	71.01	15.96	1.75	.28
Colorado	2	4.17	6.62	66.82	20.03	2.36	.38
Washington Territory	1	5.20	7.16	67.37	18.34	1.93	.31
Oregon	1	5.12	4.80	68.37	19.96	1.75	.28
California	1	4.20	6.02	71.63	16.40	1.75	.28

The chemical composition of the specimens appears from the preceding data to be rather surprising. It was reasonable to suppose that as oats deteriorate so readily, and are apparently so easily influenced by their environment, as great variations would be found in their composition under different climatic conditions as is the case with wheats, and as would correspond to the great differences in the physical character of the samples. From the one hundred and sixty-six analyses which have been made, we learn that there is not that variation in the oat kernel itself which was expected to be due to climatic condition. The proportion of husk to kernel and the compactness of the grain prove to be the all-important factors, and the weight per bushel the best means of judging of the value of the grain.

The only peculiarities noticed are that the eighteen specimens from the Pacific slope are lower in albuminoids and richer in fibre than the averages for other parts of the country. The average for the hulls from the West shows the presence of more ash than in those from the East, and more fibre, and, like the kernels, they are slightly deficient in albuminoids. Actual analysis of the mixed remainder from the individual analyses of the hulls furnished the following results:

	North. Per cent.	South. Per cent.	West. Per cent.
Water,	7.71	7.83	8.10
Ash,	5.57	5.50	6.22
Oil,	.79	.74	1.01
Undetermined,	62.47	63.84	60.09
Crude fibre,	20.83	19.64	21.45
Albuminoids,	2.63	2.45	3.13
	100.00	100.00	100.00

The small number from the West contained rather more albuminoids than the average results for that part of the country, but for the other sections there is a close agreement. In these samples, oil was determined and found to be extremely small in amount, following the percentage of albuminoids, the largest amount of both of these constituents being in the Western hulls, and there seems to be a more or less intimate connection between them.

Of all the cereals this is the richest in oil and albuminoids, the average for the former being 8.14 per cent. and for the latter 14.31; of course diminished relatively in the grain as fed, the average composition of which would probably be, as calculated from the average for each portion—

	Kernel. Per cent.	Hull. Per cent.	Whole grain. Per cent.
Water,	4.85	1.57	6.42
Ash,	1.50	1.68	3.18
Oil,	5.70	.24	5.94
Carbhydrates,	46.96	20.41	67.37
Crude fibre,	.97	5.36	6.33
Albuminoids,	10.02	.74	10.76
	70.00	30.00	100.00

An average of 20 analyses of oats in the husk given by Brewer and 153 given by Koenig is given as follows for comparison:

	Brewer. Per cent.	Koenig. Per cent.	Richardson. Per cent.
Water,	10.56	12.37	6.42
Ash,	2.95	3.02	3.18
Oil,	4.97	5.23	6.64
Carbhydrates,	61.10	57.78	66.67
Crude fibre,	9.01	11.19	6.33
Albuminoids,	11.41	10.41	10.76

The average albuminoids in the grains as fed, calculated in this same manner, are as follows for different sections:

Northern States, . . .	10.96 per cent.
Southern States, . . .	10.66
Pacific Slope, ...	9.60
Atlantic Slope, ...	10.76
Western States, . . .	11.24

The lowness of the Pacific slope is purely climatic, as has been found to be the case with all the cereals. In appearance the oats from that section are the finest. The fullness of the husk in the Western States or the plumpness of the grain makes this the richest in albuminoids as it is fed. The South is poorest, for reasons which have been mentioned. That these figures are entirely dependent on the percentage of husk, and not on peculiarities of the kernel, a study of their analyses will show; for, among 179, only 3 fell below 10 per cent. of albuminoids, 4 below 11 per cent., and 12 below 12 per cent., while at the same time only 13 are above 17 per cent., and 23 above 16 per cent.; that is to say, all but 28, or 84.4 per cent., are within the limits of 12 and 16 per cent., a small variation, although the albuminoids are higher in amount than wheat; and as the averages for the different States and sections of the country do not vary far from 14.3 per cent., with the exception of the Pacific coast, oats cannot be said, as far as the grain itself is concerned, to be in chemical composition very susceptible to their environment, although extremes widely apart are found.

These were as follows:

Extremes in Composition of Kernels of Oats.

	Highest.	State.	Lowest.	State.
	Per cent.		Per cent	
Water.........	11.13	Montana..................	4.67	Arkansas.
Ash......... ...	2.94	Michigan..................	.87	Iowa.
Oil.............	11.20	Texas.....................	6.50	Virginia.
Carbhydrates	71.91	North Carolina	62.82	Texas and Missouri.
Crude fibre...	2.08	Kentucky and Oregon	.88	South Carolina.
Albuminoids.	19.44	Ohio.......................	9.10	North Carolina.

The highest percentage of albuminoids was 1.41 per cent. higher than has been found in any other cereal in this country, and the lowest 2 per cent. higher than the lowest percentage in wheat.

The analyses of the heaviest and largest, of those having the greatest and least weight per bushel, of those having highest and lowest percentage of albuminoids, and of the smallest in size and in weight per bushel, have been selected as a study of the effect of these contrasts on the chemical composition.

Composition of Specimens Exhibiting Extreme Characteristics.

	Serial number.	State.	Weight of 100 kernels.	Husk.	Weight per bushel.	Water.	Ash.	Oil.	Carbhydrates.	Crude fibre.	Albuminoids.
			grams	per ct.	lbs.	p. c.	p. c.	p. c.	p. c.	p. c.	p. c.
Smallest....................	3200	Nebr...	1.512	31.21	29.7	7.32	2.24	8.72	66.39	1 33	14.00
Largest	3277	Oreg...	3.786	40.85	43.3	7.01	2.42	7.87	66.80	2.07	13.83
Cleanest....................	3041	Fla.....	2.880	32.87	31.5	5.83	2.52	7.68	68.93	1.56	13.48
Chaffiest	3185	Miss...	2 113	25.40	38.2	7.05	2.10	7.81	67.32	1.54	14.18
Highest per cent. of kernel	3435	Wash .	3.148	20.72	43.2	6.55	1.55	10.57	68.36	1.07	11.90
Lowest per cent. of kernel	3391	Dak...	2.372	44.63	38.8	8.75	2.15	9.47	66.17	1.56	11.90
Highest albuminoids......	3262	Ohio..	2.670	39.17	40.0	6.78	2.07	7.40	63.21	1.10	19.44
Lowest albuminoids......	3249	N. C..	2.060	29.50	47.8	7.78	2.02	7.32	71.91	1 87	9.10
Heaviest weight per bushel	3020	Col....	2.958	30.24	48.3	4.80	2.08	7.27	66.82	1.00	18.03
Lightest weight per bushel	3002	Ala....	3.068	31.66	24.7	6.59	1.80	8.98	66.20	1.20	15.23
Average weight for U. S...	....	U. S...	2.507	30.03	37.2	6.93	2.15	8.14	67.09	1.38	14.31

From the preceding figures nothing can be deduced which shows any such difference as we might expect between the largest and smallest oats, between the cleanest and most chaffy, or between those having the highest and lowest proportion of kernel in the grain. The weight per bushel of the specimen having the lowest percentage of albuminoids is extraordinarily high, while that containing the highest percentage is also above the average. Differences, too, between the weights per bushel of the extreme specimens are in nowise connected with their chemical composition. The largest and one of the finest and heaviest oats from Oregon had nearly the maximum of husk, and, while the lowest proportion of husk corresponded, of course, with a high weight per bushel, the largest proportion of husks was coincident with a weight per bushel above the average.

An immense number of conditions seem, therefore, to affect the characteristics of this grain, and while in many ways, at first glance, from its chemical composition, it seems to be less changeable than one would expect, on examination it seems to be quite largely influenced by all the circumstances of its environment, and more especially in its physical character.

The investigation has extended only to the crop of one year, and it would be necessary, for a thorough knowledge of the habits of this cereal, to follow it in a number of localities for a series of years, as has been done with wheat.

Maercke, in Germany, has followed out this subject under the conditions there existing, and has published some extremely interesting results in the *Zeitschrift des landwirthschaftlichen Verein der Provinz Sachsen*, which are worthy of careful study.

WASHINGTON, D. C., *May*, 1886.

Vol. VIII. [December, 1886.] No. 6.

AMERICAN CHEMICAL JOURNAL.

ON THE ACTION OF AMMONIA ON ACETONEDICARBONIC ETHYL ESTER. SYNTHESIS OF PYRIDINE DERIVATIVES.[1]

By H. N. Stokes and H. Von Pechmann.

Acetonedicarbonic acid[2] and ammonia react violently; the products have not been isolated. Alcoholic ammonia appears to be almost without action on *acetonedicarbonic ethyl ester* in the cold; on heating, carbon dioxide is split off, forming ammonium carbamate and other not examined products.

The action of aqueous ammonia on the ether is much smoother, two bodies being formed, according to the conditions observed. If the ester is mixed with ordinary aqueous ammonia, and cooled with ice, a deposit of colorless needles is formed. When removed from the mother liquor this body fuses at a low temperature (under 15°), and cannot again be got to solidify. Apparently the same substance is formed by passing ammonia gas into the ester, pure or diluted with ordinary ether. The substance is quite readily soluble in ether and alcohol, and is decomposed instantly by acids into ammonia and acetonedicarbonic ethyl ester. It was not analysed, but is probably the analogue of the ammonia derivative of acetacetic ester,[3] when crystallised perhaps $C(OH)(NH_2)(CH_2.CO_2C_2H_5)_2$, and when liquid $C(NH)(CH_2.CO_2C_2H_5)_2$.

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[1] Preliminary Notice, Berichte **18**, 2290.

[2] Von Pechmann, Berichte **17**, 2542.

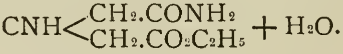
[3] Collie, Liebig's Annalen **226**, 298.

A much more stable body is formed by longer action of very concentrated aqueous ammonia on the ester. The ester used must be nearly pure, such as that obtained by saturating a mixture of equal parts acetonedicarbonic acid and alcohol with hydrochloric acid gas, diluting, and extracting the ester with ether. That obtained by adding alcohol to the direct product of the action of sulphuric on citric acid[1] has proved absolutely useless for this purpose.

To 1 volume acetonedicarbonic ester contained in a wide-mouthed bottle and cooled in ice and salt is added carefully, to prevent mixing, 1 volume of aqueous ammonia saturated in a freezing mixture. The bottle is then tightly closed and the contents mixed. If the mixture separates into two layers, more ammonia must be passed in, with cooling, until perfect solution is obtained. Crystals of the above-mentioned easily fusible compound are deposited, but some disappear. After standing two days at ordinary temperature the contents of the bottle become converted into a firm mass of greenish crystals, which are sucked out in a funnel with the pump and dried on porous plates. More may be obtained by allowing the strongly ammoniacal filtrate to stand in the open air in shallow vessels. The brown mass is washed with ether and recrystallised from water, avoiding too long heating. The snow-white product is freed from the dark fluorescent mother liquor by washing in a funnel with a little cold water. Thus obtained it is nearly pure, but becomes brownish by long keeping. After two or three recrystallisations from water it is perfectly pure, and may be kept without change indefinitely. The yield is about 70 per cent. of the theoretical.

	Calculated for $C_7H_{14}N_2O_4$.	Found.	
C	44.21	44.10	44.24
H	7.37	7.32	7.35
N	14.74	14.52	14.41

The properties of the body agree with the formula



$$CNH<\begin{matrix}CH_2.CONH_2\\CH_2.CO_2C_2H_5\end{matrix} + H_2O.$$

Whether the water is crystal water could not be decided. On gently heating, water and ammonia are given off simultaneously. It may be designated *β-imidoglutamic ethyl ester.*[2]

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[1] Berichte **18**, 468 Ref.

[2] The name β-oxyamidoglutamic ethyl ester, first adopted, Berichte **18**, 2291, is rejected, as no proof of the existence of hydroxyl in the body has been obtained.

The body forms long, flat, colorless, flexible needles. It fuses at 86°, and if heated higher, gives off water and ammonia. It is difficultly soluble in cold, readily in hot water and in alcohol, moderately in hot chloroform and difficultly in ether. Ferric chloride colors its solution deep red. Its aqueous solution soon decomposes, giving off ammonia and becoming yellow, and leaving on evaporation a greenish substance insoluble in alcohol. Cold dilute acids dissolve it, splitting off ammonia. Platinum chloride at once produces ammonium chloroplatinate. From its solution in dilute hydrochloric acid ether extracts a small quantity of a body fusing at 61°, and giving a purple color with ferric chloride. Sodium nitrite, added in excess to its acid solution, produces a precipitate, which, recrystallised from water or alcohol, forms small yellow needles, fusing at 178°, with evolution of hydrocyanic acid, etc. It appears to be an isonitroso-compound, but the few analyses made did not agree with any probable formula. It dissolves in alkali, but not in dilute acids, and gives no reaction with phenol and sulphuric acid.

Glutazine[1] *or Dioxyamidopyridine.*

β-Imidoglutamic ethyl ester is insoluble in cold solutions of alkalis or alkaline carbonates. By boiling with a carbonate it is decomposed, partly according to the reaction

$$C_7H_{14}N_2O_4 = C_5H_6N_2O_2 + C_2H_6O + H_2O.$$

One part substance is boiled with one part crystallised soda and 3—4 parts water for about ten minutes, or until a sample on cooling gives no crystals on rubbing the inside of the tube with a glass rod. On acidifying the cooled liquid with acetic acid a nearly colorless crystalline powder is thrown down, which is washed with cold water and alcohol. Thus prepared it is practically pure, but may be once recrystallised from water. The yield is about 40 per cent. of the theoretical. The remainder of the ester appears to undergo deeper decomposition, ammonia being given off and products formed which could not be isolated.

	Calculated for $C_5H_6N_2O_2$.	Found.	
C	47.62	47.62	47.34
H	4.76	4.84	4.77
N	22.22	22.68	22.33

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[1] Berichte **18**, 2291.

αα′-Dioxy-γ-amidopyridine forms colorless rectangular plates, or bunches of pointed crystals with serrated edges, sometimes also comb-like aggregates resembling sal ammoniac. When precipitated from its alkaline solution it forms a heavy, sandy powder. Frequently it has a greenish or yellowish tint, which cannot be removed by recrystallising. It fuses above 300°, with total decomposition and evolution of ammonia, leaving a very difficultly combustible coal. It is difficultly soluble in cold, moderately in hot water, nearly insoluble in hot alcohol, and insoluble in all other neutral solvents and acetic acid. Its reaction is acid. No ammonia is evolved on boiling with concentrated alkalis. It has acid properties, decomposing soluble or insoluble carbonates on boiling, forming salts which are decomposed in the cold by carbonic acid. These salts oxidise slowly in the air, especially when their solutions are heated, forming a dark green substance, which dissolves in warm acids, the solution being red when viewed by transmitted light in thick layers, but green when in thin layers or when dilute. Alkalis change this to a fine purple. Glutazine is also a base, dissolving in cold dilute mineral acids without decomposition. Cold concentrated acids, except nitric, do not decompose it. On warming, the dilute nitric acid solution is oxidised; that in hydrochloric or sulphuric acids is decomposed into ammonia and, in the former case, trioxypyridine; in the latter, trioxypyridine anhydride. Its neutral solution gives, in the cold, with ferric chloride a deep red color, which, on warming, becomes dark green, remaining clear (characteristic). No pyridine was obtained by distilling with zinc dust.

The *hydrochlorate* is obtained by dissolving the body in cold concentrated hydrochloric acid. The salt at once crystallises out as colorless prisms, readily soluble in alcohol, but soluble without decomposition only in water containing free hydrochloric acid.

	Calculated for $C_5H_6N_2O_2.HCl + H_2O$.	Found.
Cl	19.67	19.54

It is permanent over sulphuric acid; but loses most of its water at 100°, a small part reacting to form ammonium chloride, etc.

The *sulphate* forms colorless prisms, moderately soluble in water containing free acid.

The *sodium*, *ammonium* and *barium* salts are extremely soluble in water, and could not be obtained pure, as they easily oxidise in the air, becoming green. The ammonium salt dissociates completely on boiling. The *silver salt* forms colorless leaflets, with much crystal water, which is lost on standing in the air. It is insoluble, and soon blackens in the light or on heating or boiling with water.

	Calculated for $C_5H_5O_2N_2Ag$.	Found.
Ag	46.35	44.61

Action of Bromine on Dioxyamidopyridine.

Dioxyamidopyridine gives a very characteristic reaction with bromine water. If a little of this reagent is added to its solution in dilute hydrochloric acid, a yellow crystalline precipitate is at once formed, which, on gently warming, becomes dark green. It also soon becomes green if exposed to the air, and hence is difficult to isolate. It dissolves in cold sodium hydroxide solution, and on acidifying crystallises out as prisms. Ammonia converts it into a white insoluble substance. It also dissolves in hot alcohol. The green substance is insoluble in water, alcohol, acids, or alkalis, but is instantly reduced by warming with stannous chloride, forming an insoluble yellow body, which again becomes green by warming with bromine water. These reactions have not been further studied. If bromine water is added to the acid solution *in excess*, till no further decolorisation occurs, the yellow body at first formed redissolves, and in a short time the solution becomes filled with colorless needles. These were several times recrystallised from chloroform and analysed. This serves to detect dioxyamidopyridine (and trioxypyridine) in quite dilute solutions.

	Calculated for $C_4H_2Br_5NO_2$.	Found.	
C	9.68	9.81	
H	.40	.56	
N	2.82	3.34	3.34
Br	80.64	81.99	79.82

Owing to its instability the substance is difficult to purify sufficiently for analysis, but its decompositions prove beyond doubt the formula $C_4H_2Br_5NO_2$. It forms beautiful colorless needles or prisms. Its fusing point, because of its instability, cannot be obtained constant; in the most favorable cases it was 148°, but often much lower. Heated higher it gives off bromine and hydrobromic acid. It is insoluble in cold water; readily in alcohol, which slowly decomposes it on heating; readily in ether and glacial acetic acid; moderately in cold, readily in hot benzene; moderately in hot chloroform, and insoluble in ligroin. It is instantly decomposed by alkalis, but is insoluble in cold dilute acids. It is best recrystallised from chloroform; but the solution, if allowed to stand too long, contains free bromine. Its nature is explained by its decomposition with water and alcoholic ammonia.

Some of the body was boiled with water in a flask provided with an inverted condenser, a current of air free from carbon dioxide being passed through, and into a flask of baryta water. On boiling, oil drops appeared in the liquid, and barium carbonate was formed in the baryta water. After about ten minutes' boiling the oil was drawn off, and found to have the odor and boiling point of *bromoform*, and gave the isonitrile reaction with aniline. The concentrated aqueous solution deposited crystals, which, after recrystallisation, fused at 154° and showed the other properties of *dibromacetamide* (m. pt. 156°).

	Calculated for $CHBr_2.CONH_2$.	Found.
C	11.06	11.42
H	1.38	1.48
N	6.45	6.80

Dibromacetamide sublimes readily without decomposition; is moderately soluble in cold, easily in hot water, alcohol, ether and chloroform. The body $C_4H_2Br_5NO_2$ is totally decomposed by boiling a minute with alcoholic ammonia. On cooling, crystals were deposited, which, after several recrystallisations from alcohol, formed octahedra fusing at 200.5° and agreeing with the description of *dibrommalonamide*, which fuses at 206°.[1] The yield was good.

	Calculated for $CBr_2(CONH_2)_2$.	Found.	
C	13.85	14.42	13.96
H	1.54	1.70	1.66
N	10.75	11.09	

It may be mentioned that dibrommalonamide has a persistent disagreeable sweet taste, accompanied by a sensation of irritation in the mouth and throat. The alcoholic ammoniacal solution contained bromoform and a small quantity of a body fusing at 100°–103°. These decompositions are easily explained, if we regard the body $C_4H_2Br_5NO_2$ as the *amide of pentabromacetacetic acid* (or pentabromacetylacetamide) $CBr_3.CO.CBr_2.CONH_2$.

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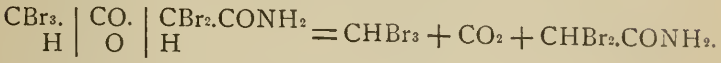
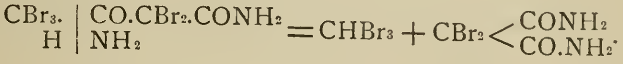
[1] Freund, Berichte **17**, 783.

I. With water—



$$\begin{array}{r|c|l} CBr_3. & CO. & CBr_2.CONH_2 \\ H & O & H \end{array} = CHBr_3 + CO_2 + CHBr_2.CONH_2.$$

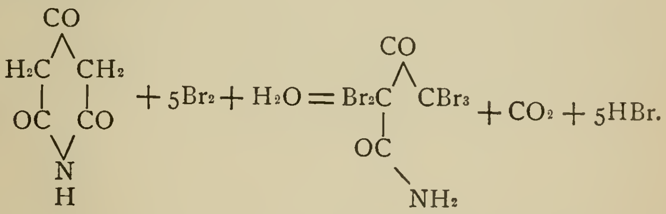
II. With alcoholic ammonia—



$$\begin{array}{r|l} CBr_3. & CO.CBr_2.CONH_2 \\ H & NH_2 \end{array} = CHBr_3 + CBr_2{<}\begin{array}{l} CONH_2 \\ CO.NH_2 \end{array}.$$

The action of aqueous ammonia takes place in another direction, which was not studied.

Trioxypyridine, under similar circumstances, also gives pentabromacetylacetamide. We may therefore regard the action of bromine on dioxyamidopyridine as taking place thus, after separation of ammonia:



Action of Acetyl Chloride on Dioxyamidopyridine.

Dioxyamidopyridine and acetyl chloride readily react: best by heating in a sealed tube at 100°–120°. On cooling no hydrochloric acid escapes, and nothing is dissolved in the excess of the reagent. The product is a colorless crystalline mass, chiefly the hydrochlorate of *monoacetyldioxyamidopyridine*. It could not be recrystallised without partial decomposition, and was analysed after drying at 120°.

	Calculated for $C_5H_5(C_2H_3O)N_2O_2.HCl$.	Found.	
C	41.08	40.10	41.14
H	4.40	4.74	4.80
N	13.69	12.48	

It is readily soluble in alcohol, but is decomposed by water.

The free acetyl compound is obtained by decomposing the above salt by sodium acetate, and purified by recrystallising from water.

	Calculated for $C_5H_5(C_2H_3O)N_2O_2$.	Found.
C	50.00	49.58
H	4.76	4.96
N	16.67	16.42

Monoacetyldioxyamidopyridine closely resembles dioxyamidopyridine, but is somewhat less soluble in water and more soluble in alcohol. It crystallises from water in small lustrous plates, which, when pure, are colorless, but usually have a greenish tint. It begins to blacken at about 230°, and fuses at 285°–290°. Its solution gives no color in the cold with ferric chloride, or at most a faint brown. On boiling it becomes violet. It is difficultly soluble in acids, but readily in alkalis. It does not react with hydroxylamine. It is a monobasic acid. The *ammonium salt* crystallises from its solution in excess of warm ammonia in transparent hexagonal plates. It is moderately soluble in cold water, insoluble in alcohol, and on gently heating gives off water and ammonia.

	Calculated for $C_5H_4(C_2H_3O)N_2O_2,NH_4 + H_2O$.	Found.
C	41.38	41.86
H	6.40	6.66
N	20.69	20.56

The *barium salt* is easily soluble in water. The *silver salt* is insoluble and unstable.

The position of the acetyl has not been decided. The fact that bromine water does not give the colored products obtained from dioxyamidopyridine, which evidently depend on the presence of the imido group, and its neutrality towards hydroxylamine, make it probable that it replaces the imide hydrogen. It decolorises bromine water but slightly, and the product, fine needles, is not identical with pentabromacetylacetamide.

By boiling with acetic anhydride a higher acetyl derivative appears to be formed, which remains as a syrup on evaporating, from which nothing crystalline could be obtained. Alkalis decompose it instantly, giving the monoacetyl compound.

Action of Hydroxylamine on Dioxyamidopyridine.

Dioxyamidopyridine reacts readily with hydroxylamine, ammonia being split off and a monoxime formed, the reaction taking place equally in alkaline, neutral or acid solution. The oxime is readily obtained by heating a solution of dioxyamidopyridine to boiling with excess of hydroxylamine hydrochlorate. On cooling it crystallises out, and is pure after once recrystallising from water. It contains 1 mol. crystal water, which escapes slowly spontaneously, or rapidly by heating at 100°.

	Calculated for $C_5H_5O_2(NOH)N + H_2O$.	Found.
H_2O	11.25	11.56

The anhydrous substance gave—

	Calculated for $C_5H_5O_2(NOH)N$.	Found.
N	19.72	19.77

The crystallised oxime is a heavy, colorless sand, consisting of transparent hexagonal plates; on losing its water it becomes whiter. It blackens slowly above 150°, and fuses at 194°–196°, with sudden evolution of gas. It is difficultly soluble in cold, moderately in hot water, less soluble in alcohol, nearly insoluble in ether, and insoluble in chloroform. The aqueous solution soon becomes red. Ferric chloride gives in the cold no color; on warming, a brown, turbid solution. It dissolves in alkali and is reprecipitated by dilute acids, in which it is nearly insoluble. The alkaline solutions are often at first nearly colorless, but on standing or heating give various colors, depending on the nature and concentration of the alkali. Strong sodium carbonate solution gives a blue color, passing into brown and then red on heating. Very dilute ammonia gives a yellow-red solution, which, on warming, changes to a splendid purple, so intense that one milligram distinctly colors several litres of water. The oxime forms salts with mineral acids. It is insoluble in concentrated hydrochloric acid, which converts it into a salt crystallising in rhombic plates, soluble in alcohol, but decomposed by water. It loses its acid slowly at 90°.

	Calculated for $C_5H_5O_2(NOH)N.HCl$.	Found.
Cl	19.89	19.17

The oxime is readily decomposed by boiling with concentrated hydrochloric acid into hydroxylamine and trioxypyridine.

All attempts to introduce a second oximide group by long heating in neutral or slightly acid solution failed.

An analogous compound is formed with phenylhydrazine, with separation of ammonia. It will be described below. (See trioxypyridine.)

Action of Acids on Dioxyamidopyridine.

Weak acids, such as acetic, have no action on dioxyamidopyridine. It is readily oxidised by strong nitric acid in the cold, and by dilute nitric acid on warming. Boiling hydrochloric acid converts it into ammonia and *trioxypyridine;* boiling dilute sulphuric acid into ammonia and *trioxypyridine anhydride*, $C_{10}H_8O_5N_2$.

αα'γ-Trioxypyridine.—By boiling for 3—4 minutes with concentrated or moderately dilute hydrochloric acid, dioxyamidopyridine is completely decomposed according to the equation

$$C_5H_6O_2N_2 + HCl + H_2O = C_5H_5O_3N + NH_4Cl.$$

An estimation of the ammonia formed showed that it contains one-half the total nitrogen of the body.

Calculated for 1 atom N.	Calculated for 2 atoms N.	Found.
11.11	22.22	10.71

The separation of the other product presents some difficulties. The following method was finally adopted:

Dioxyamidopyridine is boiled with excess of concentrated hydrochloric acid for 3—4 minutes, and the solution evaporated as quickly as possible on the water bath in large watch glasses. The quantity of dioxyamidopyridine to each watch glass should not exceed two grams, as otherwise the evaporation takes too long and secondary products are formed, which cannot be removed. The dry residue, after pulverising, is covered with cold absolute alcohol, which dissolves the trioxypyridine hydrochlorate readily, leaving the sal ammoniac. The alcoholic filtrate is quickly evaporated to a thick syrup on the water bath, in not too great quantities, as here, too, secondary products are formed. The thick syrup is diluted with about 2 parts water for each part glutazine, and a solution of caustic soda (.3 part for 1 part glutazine) in twice its weight of water added, with cooling. This should just decompose the hydrochlorate, without causing precipitation of sodium chloride, or holding too much trioxypyridine in solution. A thick mass of crystals soon forms, which is sucked out, pressed on a porous plate, washed on another plate with a little water, and dried. The product is yellowish, and should leave no ash.

	Calculated for $C_5H_5O_3N$.	Found. I.	Found. II.
C	47.24	46.37[1]	47.00
H	3.94	4.23	4.36
N	11.02	10.54	10.81

[1] Analysis of a preparation not quite free from inorganic matter.

$\alpha\alpha'\gamma$-*Trioxypyridine*, thus prepared, is a heavy yellowish sandy powder, consisting of microscopic prisms or needles. Heated above 100° it slowly becomes yellower, and at 220°–230° swells up with only partial fusion, gives off water, and becomes orange-colored. When dry it is permanent, but when moist, and especially when heated in solution, it rapidly changes. It is moderately soluble in cold, readily in hot water, and insoluble in all other neutral solvents. It does not readily recrystallise from its concentrated aqueous solution, and cannot be purified in this way. On evaporating a brownish mass is obtained, containing unaltered trioxypyridine, its anhydride, $C_{10}H_8O_5N_2$, and other substances. With ferric chloride it gives a deep red color, which, on standing or warming, becomes yellow. Barium chloride and ammonia give no precipitate. These two reactions distinguish it from the trioxypyridine or pyromekazonic acid of Ost,[1] which gives an indigo-blue color with ferric chloride and a blue precipitate with the latter reagents. Bromine water gives no precipitate unless added in excess, when *pentabromacetylacetamide* (see above) is formed. Heated with zinc dust it carbonises for the greater part, the distillate containing ammonia and pyridine, which was recognised by its odor, but not obtained in quantity sufficient for separation and analysis.

Trioxypyridine has a strong acid reaction, and decomposes carbonates in the cold, giving salts which are not decomposed by carbonic acid. It appears to be monobasic. The alkaline and earthy salts are very soluble in water, and their solutions soon become dark green in the air.

The *ammonium salt*, obtained by evaporating its ammoniacal solution in a vacuum over sulphuric acid, forms thick prisms, which could not be obtained colorless. The *barium salt* was obtained and analysed in solution only by dissolving a known weight of trioxypyridine in baryta water, precipitating excess by carbonic acid and estimating barium in the filtrate.

	Calculated for $(C_5H_4O_3N)_2Ba$.	Found.
Ba	35.22	36.02

The *silver salt* is insoluble and unstable. The *hydrochlorate* forms needles easily soluble in water and alcohol, and partially decomposing on evaporation into ill-defined products.

Trioxypyridine has decidedly the properties of a ketone, as shown by its reaction with hydroxylamine, phenylhydrazine and ammonia. On warming with hydroxylamine hydrochlorate it gives an oxime fusing at 194°–196°, and in every respect identical with that obtained from dioxyamidopyridine, which was confirmed by analysis.

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[1] Jour. pr. Chem. [2] **19**, 204; **27**, 258.

	Calculated for $C_5H_5O_2(NOH)N + H_2O$.	Found.
H_2O	11.25	11.22

	Calculated for $C_5H_5O_2(NOH)N$.	Found.
N	19.72	19.80

Phenylhydrazine Derivative.

To obtain this it is not necessary or desirable to isolate the trioxypyridine. One part dioxyamidopyridine is decomposed by boiling with hydrochloric acid, and to the diluted solution one part phenylhydrazine and sodium acetate are added. The body crystallises out at once, and may be recrystallised from alcohol.

	Calculated for $C_5H_5O_2(N_2HC_6H_5)N$.	Found.
N	19.35	19.75

It may also be obtained directly from dioxyamidopyridine, ammonia being evolved. It forms colorless plates closely resembling glutazine. It begins to blacken at 220° and fuses at 230°, with violent evolution of gas. It is difficultly soluble in hot water, difficultly in cold, readily in hot alcohol, scarcely soluble in dilute acids, readily in alkalis.

Formation of Dioxyamidopyridine from Trioxypyridine.

If fused with excess of crystallised ammonium acetate for 3—4 minutes at 120°–140°, trioxypyridine is quantitatively converted into dioxyamidopyridine, which remains, on adding alcohol, as a greenish powder, giving the characteristic reactions with ferric chloride and bromine water. After recrystallising it was analysed.

	Calculated for $C_5H_6O_2N_2$.	Found.
N	22.22	22.33

The synthesis cannot be effected by simply evaporating with ammonia.

Trioxypyridine Anhydride.

This is the chief product of the decomposition of dioxyamidopyridine with boiling dilute sulphuric acid, and is best isolated as its acid barium salt. It is very stable, and may be prepared in any quantity in one operation. Dioxyamidopyridine is boiled for five minutes with twenty parts of ten per cent. sulphuric acid, the hot solution supersaturated with concentrated baryta water, filtered from barium sulphate, and boiled until the ammonia is driven off, which should be done in a flask, as otherwise partial oxidation occurs. The solution, containing the neutral barium salt and free baryta, is slightly acidified with acetic acid, which throws down the acid salt, and left to stand a few hours until the crystallisation is complete. The product is purified by twice dissolving in baryta water and precipitating with acetic acid. The *acid barium salt* thus obtained forms a yellow precipitate, or, when obtained from dilute solutions, groups of small yellow prisms. It is insoluble in water, alcohol and dilute acetic acid, but is decomposed by mineral acids, and dissolved by alkalis. It contains four molecules crystal water, two of which escape over sulphuric acid, the other two only on heating to 180°.

	Calculated for $(C_{10}H_7O_5N_2)_2Ba + 4H_2O$.		Found.	
$2H_2O$	5·30	5·37	5·33	5·38
$2H_2O$	5·30		5·38	
Ba	20.18	20.04	20.14	
N	8.25	8.14		

To isolate the anhydride, the acid barium salt is boiled with excess of concentrated hydrochloric acid, evaporated to dryness on the water bath, again moistened with concentrated acid, and dried. The pulverised residue is covered with absolute alcohol, which dissolves the hydrochlorate, leaving barium chloride. The alcoholic solution is evaporated, a little water added, and again evaporated, and this is repeated three or four times, or until no more hydrochloric acid is given off. The crystalline residue is boiled with a little water, which removes a greenish impurity.

	Calculated for $C_{10}H_8O_5N_2$.	Found.	
C	50.85	50.05	50.62
H	3·39	3·56	3·73
N	11.86	11.86	11.98

Trioxypyridine anhydride, thus prepared, is a loose mass of flesh-colored microscopic prisms. It is very stable, and fuses only at high temperature, with decomposition. It dissolves but slowly in boiling water, and is insoluble in other neutral solvents and in glacial acetic acid. It is readily soluble only in excess of alkali baryta water, or alkaline carbonates, which it decomposes in the cold. It dissolves difficultly in concentrated hydrochloric acid forming the *hydrochlorate*, which is soluble in alcohol and crystallises in needles, but is decomposed by water, forming a jelly which loses all its acid on evaporating, leaving it in the crystalline form. The *sulphate* also forms needles, and is similarly decomposed by water. Its power of gelatinising is very great, and is due to the presence of its own or other salts, which must be removed before it can crystallise. In the pure state it does not gelatinise, but separates from its solution in hot water as small prisms. The jelly does not crystallise by long standing. Under some circumstances it is partly precipitated as an amorphous flocculent mass.

The *acid sodium salt* forms yellow prisms, rather more soluble than the corresponding barium salt.

The *acid ammonium salt* forms yellow crystals, difficultly soluble in cold water.

The *acid silver salt* is insoluble.

None of these are decomposed by acetic acid.

The *neutral* alkaline and earthy salts have the formulas $C_{10}H_6O_5N_2M'_2$ and $C_{10}H_6O_5N_2M''$ and are easily soluble in water, the solution gradually oxidising in the air. They are not decomposed by carbonic acid ; acetic acid throws down the acid salt.

The *neutral barium salt* is difficult to obtain pure in solid form. Its solution, obtained by dissolving a known weight of anhydride in baryta water, precipitating excess by carbonic acid, and determining barium in the filtrate, gave

	Calculated for $C_{10}H_6O_5N_2Ba$.	Found.
Ba	36.81	36.93

The *neutral silver salt* is insoluble.

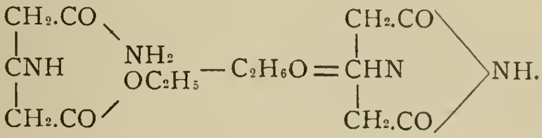
No salts containing more metal could be obtained.

Trioxypyridine anhydride reacts under no conditions with hydroxylamine. An imido group could not be introduced by fusing with ammonium acetate, which gives simply the acid ammonium salt. Phenylhydrazine does not act on it in the cold ; on boiling, a red substance soluble in alkali was obtained.

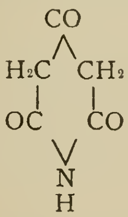
Bromine water produces a precipitate of flesh-colored needles, not decomposed by boiling water. The anhydride cannot be decomposed into trioxypyridine by boiling with acids or alkalis, but is formed from it by evaporating its aqueous solution.

Constitution of the Above Bodies.

From its formation from β-imidoglutamic ethyl ester the two oxygen atoms of dioxyamidopyridine must occupy the $\alpha\alpha'$-, and the amido or imido group the γ-position.



Whence follows the symmetrical $\alpha\alpha'\gamma$ arrangement for trioxypyridine, which is therefore the analogue in the pyridine series of phloroglucine, dioxyamidopyridine being the analogue of phloramine. The ease with which the γ-oxygen reacts with hydroxylamine, phenylhydrazine and ammonia proves beyond doubt that it exists in the ketone form, which is confirmed by the studies of Haitinger and Lieben[1] on the derivatives of γ-oxypyridine. Whether the $\alpha\alpha'$-oxygen atoms exist as carbonyl or hydroxyl is not so readily decided. Their neutrality towards hydroxylamine cannot be regarded as proof of the latter view, as the group C—CO—NH is not known to react with it. If we assume that von Baeyer's[2] theory that rings tend to be purely secondary or purely tertiary holds in this case, and remember that α-oxypyridine is a lactam,[3] the presumption is in favor of the formulas



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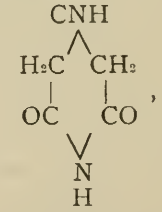

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and the bodies should be designated as *$\alpha\alpha'\gamma$-triketopiperidine* and *$\alpha\alpha'$-diketo-γ-imidopiperidine.*[4] Whether these bodies ever assume the tertiary form is questionable. The neutrality of trioxypyridine anhydride towards hydroxylamine and fused ammonium acetate may indicate the absence of the, in other cases, so easily reacting γ-carbonyl group, and that a change to the phenol form with anhydride formation has occurred, giving

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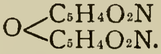
[1] Monatshefte **6**, 298.

[2] Berichte **19**, 162.

[3] Von Pechmann, Berichte **18**, 317.

[4] Von Baeyer, Berichte **19**, 161-163.



$$O<\begin{matrix}C_5H_4O_2N\\C_5H_4O_2N.\end{matrix}$$

As to whether the α- or γ-oxygen atoms are here concerned it is useless to speculate. No salts of glutazine or trioxypyridine containing more than one atom of metal in the molecule could be obtained, and this might well be associated with the pyridine nitrogen. Attempts to obtain alkyl derivatives, whose solubility or insolubility in alkalis, and possible decomposition into alkylamine by reducing agents,[1] might throw light on the subject, have not been pursued far enough to yield definite results. The silver salt of glutazine gives with ethyl iodide only a small quantity of an easily fusible body, insoluble in alkalis—probably the monoethyl ether. Considering the doubt which pertains to the subject, we have retained the older names trioxy- and dioxyamido-pyridine, not wishing thereby to commit ourselves to any decided view of the constitution of these bodies further than that indicated by the experiments above given.

Chlorine Derivatives of γ-amidopyridine.

With phosphorus pentachloride, dioxyamidopyridine yields at least four well-marked products—viz.:

1. Dichlordioxyamidopyridine, $C_5N_2H_4Cl_2O_2$.
2. Trichloroxyamidopyridine, $C_5N_2H_3Cl_3O$.
3. Trichloramidopyridine, $C_5N_2H_3Cl_3$.
4. Tetrachloramidopyridine, $C_5N_2H_2Cl_4$.

Under the conditions observed 2 and 4 were formed in large and nearly equal quantity, while the amount of 1 and 3 was very small. Monochloroxy- or dichloramido-pyridine could not be obtained. An attempt to make them by using phosphorus trichloride also led to no result.

Dioxyamidopyridine is made into a thin paste with phosphorus oxychloride, and 6—7 parts phosphorus pentachloride gradually added. When the reaction has moderated, the flask, provided with a return condenser, is heated in an oil bath for two or three hours, or until the contents form a nearly clear liquid. The oxychloride and unchanged pentachloride are then distilled off until the residue is nearly solid and the temperature of the oil about 200°–210°. Water is then added, with cooling, and the flask is left to stand until all residual oxychloride is destroyed. Bodies 2 and 4 are found mostly in the insoluble residue, and are separated by boiling with dilute alkali, which dissolves 2 only, which is then precipitated by an acid. Both are purified by several recrystallisations from alcohol. The acid filtrate from the mixture of 2 and 4, on being made alkaline, gradually deposits 3, which is recrystallised from much hot water. The alkaline filtrate, on adding acetic acid, gives needles, which may consist of 1 alone or of 1 and 2, which may be separated by dilute hydrochloric acid, in which 1 is more soluble. It is then recrystallised from water.

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[1] Von Pechmann, Berichte **18**, 317.

Whether these bodies contain the amido or imido group remains uncertain. We have provisionally assumed the former, or tertiary form, which best agrees with the properties of body 2.

Dichlordioxyamidopyridine, $C_5N_2H_4Cl_2O_2$.

	Calculated for $C_5N_2H_4Cl_2O_2$.	Found.
Cl	36.41	35.79
N	14.36	14.36

The body, recrystallised from water, forms short, flat, colorless needles, fusing, with decomposition, at 241.5°. It is difficultly soluble in hot water and alcohol, readily in alkalis or dilute hydrochloric acid. It slowly decolorises bromine water, giving a precipitate of colorless stars, soluble in boiling water. Of its constitution nothing is known except that the oxygen atoms have the $\alpha\alpha'$-, the amido or imido group the γ-positions.

Trichloramidopyridine, $C_5N_2H_3Cl_3$.

	Calculated for $C_5N_2H_3Cl_3$.	Found.
Cl	53.92	53.93
N	14.18	14.49

The body, recrystallised from hot water, in which it is difficultly soluble, forms a felt-like mass of long, delicate, colorless needles. It fuses at 157.5°, and readily sublimes unchanged. It is very soluble in alcohol, slightly in dilute hydrochloric acid, and insoluble in alkali. It is characterised by its dilute solution giving, with bromine water, a precipitate, which, after recrystallising from alcohol, forms flat colorless needles, fusing at 223°, easily sublimable and insoluble in water, acids and alkalis; probably monobromtrichloramidopyridine. The chlorine atoms must occupy the $\alpha\alpha'\beta$-positions.

Trichloroxyamidopyridine, $C_5N_2H_3Cl_3O$.

	Calculated for $C_5N_2H_3Cl_3O$.	Found.	
C	28.10	28.09	
H	1.41	1.64	
N	13.11	13.61	
Cl	49.88	50.33	50.48

The body forms flat colorless needles. It fuses at 282°, and by careful heating may be sublimed unchanged. It is almost insoluble in cold, very slightly in hot water; difficultly in cold, moderately in hot alcohol; moderately in ether; difficultly in hot benzene; insoluble in ligroin. It dissolves readily in strong hydrochloric or sulphuric acids, and is in greater part precipitated by diluting. The little remaining in solution can be extracted by ether. With ferric chloride it gives a red color only on boiling. It is not attacked by boiling with concentrated alkalis or acids, but by fusion with alkali or by heating to a high temperature with fuming hydrochloric or hydriodic acids; in the latter case the only well-marked products are carbon dioxide and ammonia. It is not acted on by hydroxylamine or bromine water. It dissolves in pure phenylhydrazine without change, but, on boiling, ammonia is evolved. Phosphorus pentachloride at 150° slowly converts it into tetrachloramidopyridine. It is also formed in small quantity by heating β-imidoglutamic ethyl ester with phosphorus pentachloride. It is a monobasic acid, decomposing soluble carbonates on gently warming. The salts are decomposed by acetic acid.

The *sodium salt* forms needles with 3—4 molecules crystal water, moderately soluble in cold water, difficultly in alcohol.

Dried at 100° it gave:

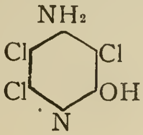
	Calculated for $C_5N_2H_2Cl_3ONa$.	Found.
Na	9.77	10.35

It forms anhydrous hair-like tufts by mixing the alcoholic solution of the free body with alcoholic sodium ethylate.

Its solution gives: with *barium chloride*, at first nothing; on standing or warming, prisms difficultly soluble in hot water; with *lead acetate*, an amorphous white precipitate; with *silver nitrate*, a flocculent precipitate, or sometimes a firm, transparent jelly.

The *ammonium salt* is completely dissociated on evaporating.

The properties of the ethyl ether of trichloroxyamidopyridine render probable the phenol form, whence the formula



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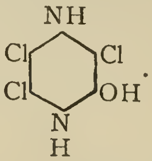
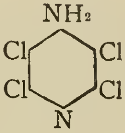


Tetrachloramidopyridine,



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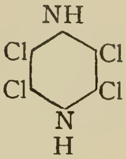

	Calculated for $C_5N_2H_2Cl_4$.	Found.
C	25.86	26.11
H	.86	1.08
N	12.07	12.34
Cl	61.21	61.39

The body forms colorless thin leaflets or nearly cubical crystals. It fuses at 212°, and sublimes without decomposition. It is insoluble in water; difficultly in cold, moderately in hot alcohol, but more so than trichloroxyamidopyridine; soluble in hot benzene. It is insoluble in alkalis, and nearly so in hot hydrochloric acid, strong or dilute. It dissolves in cold concentrated sulphuric acid, with which it may be boiled without decomposition. Alkalis attack it only on fusion.

Fuming hydriodic acid reduces tetrachloramidopyridine, giving a mixture of substances with pyridine-like odor and properties which give Hofmann's reaction.[1] In no case could complete reduction be effected. Heated in sealed tubes with fuming hydriodic acid for ten hours at 200° black needles of an iodine addition product were obtained, fusing under 80°. On dissolving in sulphurous acid and making alkaline, colorless needles were obtained, which were readily soluble in dilute acids, moderately soluble in hot water, and volatile with steam or at 100°, the vapor having a rather faint pyridine-like odor. After recrystallising they fused at 157.5°. The recrystallised product was distilled with steam and collected in two fractions, each of which fused at 158°. A chlorine determination gave 43.32 per cent.; calculated for a dichloramidopyridine, 43.56 per cent. It gave a chloroplatinate crystallising in needles, difficultly soluble in water and decomposing without fusion. It contained crystal water, which escaped at 100°.

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[1] Berichte **17**, 1908.

	Calculated for $(C_5H_2Cl_2(NH_2)N.HCl)_2PtCl_4$.	Found.
Pt	26.73	26.73

Unfortunately, not enough of the substance to confirm these results could be obtained. Its pyridine-like odor is in favor of its being simply impure dichlorpyridine. The filtrate from these crystals contained still further reduced products of intense pyridine odor.

On heating tetrachloramidopyridine with 10 parts fusing hydriodic acid, and some red phosphorus for sixty hours at 300–350°, and treating the product as above, nothing crystalline could be obtained. The distillate, a clear liquid of intense pyridine odor, was acidified with hydrochloric acid and evaporated, whereby partial dissociation occurred. The residue was extracted with cold absolute alcohol, which left much ammonium chloride. Again evaporating and extracting, a syrupy salt was obtained, a portion of which gave an oil of intense pyridine odor on dissolving in concentrated alkali. The chloroplatinate from this, after recrystallising, formed flat and apparently homogeneous prisms, resembling those of pyridine chloroplatinate, but which fused at 235–245° (the pyridine salt fuses at 236°). The quantity sufficed for but one analysis.

	Found.	Calculated for $(C_5H_5N.HCl)_2PtCl_4$.	Calculated for $(C_5H_4ClN.HCl)_2PtCl_4$.
Pt	33.50	34.41	30.60

The oil is therefore probably a mixture of pyridine with chlorpyridine. In no case was any tetrachloramidopyridine recovered. The first stages of the reduction are easy, the last very difficult.

Unfortunately it was not possible to pursue the experiments further on a scale admitting of isolating the various reduction products, but the results prove beyond doubt the pyridine nature of the whole class of bodies under consideration.

Ethers of Amidopyridine.

Tetrachloramidopyridine, boiled with excess of sodium ethylate and absolute alcohol for two hours, is entirely converted into a new compound, in which one chlorine atom is replaced by ethoxyl. The product is poured into water, the precipitated crystals distilled with steam, dissolved in a little alcohol, and precipitated by water.

	Calculated for $C_5N_2H_2Cl_3(OC_2H_5)$.	Found.	
C	34.78		35.30
H	2.90	3.12	3.17
Cl	44.10	44.20	

Trichlorethoxyamidopyridine forms colorless needles fusing at 83° and subliming unchanged. It is easily volatile with steam, and slightly at ordinary temperatures, its vapor having a characteristic, sharp, but agreeable aromatic odor. It is insoluble in water, alkalis and dilute acids; extremely soluble in alcohol, ether, benzene and chloroform; moderately in ligroin. Heated in a sealed tube with dilute hydrochloric acid (sp. gr. 1.15) at a little over 100° it is readily decomposed into ethyl chloride and the trichloroxyamidopyridine above described (m. pt. 282°).

If the anhydrous sodium salt of trichloroxyamidopyridine is heated with one equivalent of ethyl iodide and absolute alcohol at 120°, two substances are formed, one of which, not volatile with steam, was not further examined. The other, after distilling with steam, fused at 83°, and was in every respect identical with the above ethoxyl compound.

The formation of the same ether from tetrachloramidopyridine and sodium ethylate, and from a salt of trichloroxyamidopyridine and ethyl iodide, proves that in this case, as in others, the atom occupying the α-position reacts most readily. The low temperature at which these reactions occur (80° and 120° respectively, and probably lower), taken with the ease with which the ether is decomposed by dilute hydrochloric acid, renders it probable that no transference of atoms occurs, and, therefore, that trichloroxyamidopyridine and its ether contain hydroxyl and ethoxyl respectively.

Tetrachloramidopyridine is further acted on if heated with excess of sodium ethylate and absolute alcohol for 3—4 hours at 190°. The liquid, on cooling, contains crystals of sodium chloride and needles. The whole is poured into water, whereby the crystals dissolve and others appear. Without removing these, the alkaline liquid is shaken out two or three times with ether, which extracts a substance which may be purified by distilling with steam, dissolving the distilled crystals in alcohol and precipitating with water (Body A). The alkaline liquid, after extraction, is acidified with hydrochloric acid, and with deposited crystals again extracted three or four times with ether. The ether contains a body (B) which may be purified by recrystallising from very dilute alcohol. The yield of A and B was nearly equal.

Body A.

	Calculated for $C_5N_2H_2Cl_2(OC_2H_5)_2$.	Found.
C	43.02	42.40
H	4.78	5.04

Dichlordiethoxyamidopyridine forms long, colorless, flat needles, fusing at 98°, readily sublimable and volatile with steam, the odor of its vapor closely resembling that of trichlorethoxyamidopyridine. It is insoluble in water, alkalis and dilute acids; very soluble in alcohol and ether. It gives a red color on boiling with ferric chloride.

Body B.

	Calculated for $C_5N_2H_2Cl_2(OH)(OC_2H_5)$.	Found.
C	37.67	37.54
H	3.59	3.68

Dichloroxyethoxyamidopyridine forms colorless, brittle, flat needles, fusing at 161.5°, and subliming if carefully heated. It is difficultly soluble in hot water, readily in alcohol and ether. It is not volatile with steam. It is insoluble in dilute acids, but dissolves in alkalis, forming salts, of which the *sodium salt* forms lustrous rhombic plates rather difficultly soluble in cold water and decomposed by acetic acid.

The same compound is formed by heating trichloroxyamidopyridine with sodium ethylate and absolute alcohol[1] for three or four hours at 190°. Moreover, the diethoxy compound, by heating several hours with sodium ethylate and absolute alcohol at 190°, is almost completely converted into the oxyethoxy compound. Hence, as regards the positions of these groups, in the one case the hydroxyl, in the other one ethoxyl, occupies the α-position. The position of the other group could not be determined. Attempts were made to decompose the diethoxy body by hydrochloric acid, hoping to obtain the dichlordioxyamidopyridine of m. pt. 241.5°, thereby proving that the second α-chlorine atom is attacked. Experiments with acid of sp. gr. 1.14, at temperatures from 100° to 140°, showed that at the higher temperatures the body was totally decomposed into ethyl chloride, ammonia and amorphous products. At 100°–110° ethyl chloride and ammonia were also formed, but the body was largely unaltered, no dichloroxyethoxy- or dichlordioxy-amidopyridine could be detected. This, however, proves nothing, as the firmness with which the amido or imido group is held in all these cases is evidently proportional to the amount of chlorine, and it is possible that those bodies with but two atoms of chlorine may be nearly as easily decomposed by hydrochloric acid as is dioxyamidopyridine itself, and therefore would be destroyed as soon as formed.

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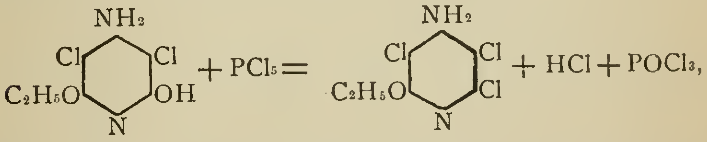
[1] This method of preparation is not to be recommended, for the decomposition is apt to go too far, or else some trichloroxyamidopyridine remains unacted on, and is not easily separated from the oxyethoxy compound.

An attempt to prove the α-position of the second ethoxy group, by heating the oxyethoxy compound with phosphorus pentachloride, thus obtaining the trichlorethoxyamidopyridine above described (m. pt. 83°), according to the equation



failed. The substance obtained resembled in odor and other properties the desired body, but fused at 175°. Considering the possibilities lying in a lactam and lactim structure, this can hardly be regarded as a *disproof* of the assumption, which must therefore be left at present undecided.

VON BAEYER'S LABORATORY, MUNICH, *August* 4, 1886.

Contributions from the Chemical Laboratory of Wesleyan University.

III.—ON THE LIBERATION OF NITROGEN FROM ITS COMPOUNDS AND THE ACQUISITION OF ATMOSPHERIC NITROGEN BY PLANTS.

By W. O. Atwater.

Experiments on the question of the assimilation of atmospheric nitrogen by plants are ordinarily made by comparing the amounts of nitrogen supplied in seed and fertilising materials with that found at the end of the experiment in the plants and in the soil or nutritive solution. If any nitrogen is found at the end of the experiment in excess of that supplied, the inference is that the excess must have come from the ambient air.

Such experiments are, however, exposed to an error resulting from the liberation of nitrogen from its compounds contained in the seed, the plant, or the food supplied. The effect of any such escape of nitrogen will be to reduce the quantity found at the end of the experiment. While, therefore, a gain is positive proof of the acquisition of nitrogen from the air, either directly by the plant through its foliage or indirectly through the medium in which the roots develop, the failure to find such acquisition is only negative proof of its non-occurrence.

In a previous communication,[1] to which this and the preceding one are supplementary, account was given of experiments by myself with peas grown in sand and supplied with certain quantities of nitrogen and other essential elements of plant food in nutritive solutions. In order to test the effect of abnormal conditions, the solutions in some of the experiments were made much more concentrated than experience has indicated to be favorable for assimilation. In some cases, furthermore, the total food-supply was made small in relation to the estimated demands of the plants, while in others it was more liberal. The quantity of nitrogen in the solutions was likewise varied, the quantity of mineral food remaining the same. Of the trials in concentrated solutions, one showed a small loss and the rest more or less gain of nitrogen. In the experiments in the moderately dilute solutions, the poorly fed plants obtained over one-third, and the tolerably well-fed ones one-half of their nitrogen from the atmosphere. It was remarked that the only considerable source of error in the experiments seemed to be in a probable loss of nitrogen by the decomposition of the nitrogen compounds of either the seeds (or plants) or the nutritive solutions, or both. It was in the hope of getting light upon this question of the loss of nitrogen that the work detailed in the previous article[1] was undertaken. The purpose of the present article, which, like the one last named, is really a continuation of the first one above referred to, is to indicate the bearing of the facts elicited upon my own and other experiments on the acquisition of atmospheric nitrogen.

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[1] This Journal **6**, 365.

INFLUENCE OF VARYING CONDITIONS UPON THE APPARENT ACQUISITION OF NITROGEN.

It will facilitate the discussion if some of the principal data which were given in detail in the first article are put together in such a manner as to show the quantities of nitrogen supplied and found, and the gain or loss under different conditions. This is attempted in Tables I and II.

TABLE I.

Statistics of Experiments on the Assimilation of Atmospheric Nitrogen by Peas.

Conditions of Experiments.			No. of Experiment.	Nitrogen supplied.			Nitrogen found at End of Experiment.			Apparent Gain + or Loss — of Nit'g'n
				In seeds.	In Nutritive Sol'n.	Total.	In Plants.	In Residual Solut'n.	Total.	
				Mgm.	Mgm.	Mgm.	Mgm.	Mgm.	Mgm.	Mgm.
Larger Nitrogen Ration.	Concentrated Solution.	Scantily fed.	8	70.3	136.9	207.2	197.5	12.7	210.2	+ 3.0
		Well fed.	6	34.8	136.9	171.7	149.6	1.2	150.8	— 20.9
	Dilute Solution.	Scantily fed.	12	68.8	136.9	205.7	260.2	45.7	305.9	+100.2
		Well fed.	10	34.6	136.9	171.5	277.8	35.7	313.5	+142.0
Smaller Nitrogen Ration.	Concentrated Solution.	Scantily fed.	7	71.5	59.4	130.9	158.1	0.0	158.1	+ 27.2
		Well fed.	5	34.2	59.4	93.6	156.1	0.0	156.1	+ 62.5
	Dilute Solution.	Scantily fed.	11	72.5	59.4	131.9	210.9	2.7	213.6	+ 81.7
		Well fed.	9	35.3	59.4	94.7	186.5	1.4	187.9	+ 93.2

The plants were grown in sand, supplied with solutions of appropriate salts including nitrogen in nitrates, and kept in open air, but protected from rain and dew. The experiments were in two series, one in each of two successive years. The second series included twelve experiments, of which Nos. 5–12 in the table suffice to illustrate the principal results obtained in the two series. The "concentrated" solutions contained from 2.5 to 6, and the "dilute" from 0.8 to 1.6 parts of water-free salts in 1000. A concentration of 1 per 1000 has elsewhere been found favorable, and one of over 2 per 1000 unfavorable to normal assimilation. The "well-fed" plants had quantities of mineral food estimated to be sufficient for their nourishment, the scantily fed ones one-half as much. The "larger nitrogen ration" was estimated to supply an amount of nitrogen rather small in proportion to the mineral food, and the "smaller nitrogen ration" less than one-half as much as the larger. The gain or loss of nitrogen is computed by adding to the amount of nitrogen in the plants that left in the nutritive solution at the end of the experiment, and subtracting from their sum the sum of the amounts in the seed and in the nutritive solution at the start. The figures for "apparent gain or loss" represent, therefore, the quantities acquired from the air less whatever may have been liberated from solution or seed or plants during growth. The nutritive solution and seed together contained from 94 to 212 mgm. and the plants from 116 to 278 mgm. of nitrogen in each experiment.

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[1] This Journal **8**, 327.

Table II.

Comparison between Apparent Gain or Loss of Nitrogen and Nitrogen Left in Nutritive Solution at End of Experiment, with Concentrated and Dilute Solutions.

Conditions of the Experiment.		No. of Experiment.	Residual Nitrogen in Solution. Estimated in per cent. of Total Nitrogen in the Solution.	Apparent Gain +, or Loss —, of Nitrogen. Estimated in per cent. of Total Nitrogen in the Plants.
With Larger Nitrogen Ration.			Per cent.	Per cent.
Concentrated Solutions	Scantily fed.	8	9.3	+ 1.5
	Well fed.	6	0.9	— 14.0
Dilute Sclutions	Scantily fed.	12	33.4	+ 38.1
	Well fed.	10	26.1	+ 51.1
With Smaller Nitrogen Ration.				
Concentrated Solutions	Scantily fed.	7	0.0	+ 17.2
	Well fed.	5	0.0	+ 40.0
Dilute Solutions	Scantily fed.	11	4.5	+ 38.7
	Well fed.	9	2.4	+ 50.0

The figures bring out very clearly the facts stated above, that in every case in which the nutritive solution was as dilute as has been found favorable for normal growth, the plants contained a large quantity of nitrogen in excess of that supplied by nutritive solution and seed—a gain which must of course have come from the air—while in cases in which, as a test of the effect of abnormal conditions, the solutions were more concentrated, there was uniformly less gain, and in one case a loss, of nitrogen. In the last case nitrogen had evidently escaped. It was natural to infer that a similar liberation of nitrogen might have occurred in the other trials with concentrated solutions. This would help to explain the small gain of nitrogen in these cases, though another cause might be sought in decreased assimilation under this abnormal condition.

A curious result of the experiments, and one which can hardly be without significance, becomes apparent when the quantities of nitrogen left in the nutritive solutions at the end of the experiments are compared with each other and with the amounts apparently acquired from the air under different conditions, as is done in Tables II and III.

The conditions most favorable for growth were with the larger nitrogen ration in the dilute solutions, experiments Nos. 12 and 10. In each of these the plants contained so much nitrogen as to show that they must have acquired large quantities from the air, and yet they left large amounts behind in the nutritive solutions. The most abnormal conditions were those of the greatest concentration—to wit, those with the larger nitrogen ration in the concentrated solutions—*e. g.*, experiments Nos. 8 and 6. In these the plants contained so little nitrogen as to make in one case a very small gain, and in the other a positive loss. In each of these latter cases, there was very little or no residual nitrogen in the solutions at the end of the experiments. In other words, in the cases in which the plants contained the most nitrogen, namely, in the normally dilute solutions, they left the most behind; but where conditions were abnormal, in the concentrated solutions, they contained the least nitrogen and left the least behind.

The cases just named were with the larger nitrogen ration. With the smaller quantities of nitrogen the differences were in the same general direction, but less marked, as may also be seen in Table II. The plants seem to have used up the smaller stock of nitrogen more quickly, or at any rate more completely, than the large stock.

The matter will be still clearer if we examine the nitrogen statistics in the cases where the differences are most marked, Nos. 6 and 10, using the original data,[1] as is done in Table III.

TABLE III.

Comparative Nitrogen Statistics of Experiments in Concentrated and Dilute Solutions.

	Expt. No. 6. Concentrated Solution.	Expt. No. 10. Dilute Solution.
	Milligrams.	Milligrams.
Nitrogen supplied in nutritive solutions	136.9	136.9
Nitrogen supplied in seed	34.8	34.6
Total nitrogen supplied	171.7	171.5
Nitrogen left in nutritive solution	1.2	35.7
Total nitrogen removed by plants and otherwise	170.5	135.8
Nitrogen contained in plants	149.6	277.8
Apparent loss —, or gain +, of nitrogen	— 20.9	+ 142.0

Or, to put it in another way:

	Under Abnormal Conditions of Growth.	Under Normal Conditions of Growth.
There were placed at the disposal of the plants.	172 mgm. N.	172 mgm. N.
The plants in some way obtained[2].	150 " "	278 " "
The plants left behind unused.	1 " "	36 " "

Grown under favorable conditions, the plants contained at maturity (278 — 172) 106 milligrams more of nitrogen than the total amount supplied, and yet left 36 milligrams behind in the nutritive solution. Grown under abnormal conditions of concentration, the plants had (172 — 150) 22 milligrams less than was furnished, and yet only left 1 milligram behind.

Comparing Nos. 8 and 12, in which the conditions of growth are similarly, though less widely, diverse, we find precisely similar, though less marked, differences of result. So with Nos. 7 and 11 and Nos. 5 and 9, where the smaller quantities of nitrogen supplied make the differences in condition less, though still analogous, the differences in result are less, but of exactly the same tenor. In other words, the plants in the more dilute solutions contained the most nitrogen, evidently got the most from the air, and, at the same time, apparently drew the least from the solutions, while those in the concentrated solutions evidently got the least from the air, had the least when mature, but yet appeared to draw most heavily upon the store in the nutritive solution.

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[1] See detailed tables in former article, above referred to, this Journal **6**, 365.

[2] *I. e.*, they contained at maturity.

That these circumstances should be entirely fortuitous, and any inferences from them fanciful, is hardly to be believed. Granting them a meaning, it can be easily explained by supposing that there was some agency at work in the experiments with concentrated solutions setting nitrogen free, and that the agency in question, be it electricity, microbes, or something else, is less effectively resisted by the plants grown in abnormal than by those in normal conditions. This accords with the fact that higher organisms resist disease, including forms commonly attributed to microbes, the more effectively in proportion as they are well nourished and in otherwise healthy condition.

But if nitrogen escaped in the trials with concentrated solutions, may it not have escaped to some extent in the other cases also? If so, the results are all inaccurate as indications of the actual acquisition of atmospheric nitrogen, and the plants must have really obtained quantities larger, by the amounts thus liberated, than the figures imply.

The data and considerations in the previous article suggest two ways in which the nitrogen might have been lost: decomposition of the nitrogenous compounds of the seeds and plants, and decomposition of the nitrates of the nutritive solutions.

In the second, third and fourth series of the experiments by Mr. Rockwood and myself on the loss of nitrogen, described in the previous article, we attempted to make the conditions as similar as practicable to those of the assimilation experiments in question, except that no food was supplied to the plants. The loss of nitrogen in the experiments of the series in which the period of growth was longest, from 14 to 52 days, was from 10 to 15 per cent. of the nitrogen of the seed.[1]

In the experiments of Boussingault,[2] referred to in the previous article, seeds of beans and maize were caused to germinate in presence of nitrates under conditions analogous to those of my assimilation experiments, and 45.3 per cent. of the nitrate was estimated by him to have been liberated during a period of 21 days. With maize the loss of nitrogen was still greater. Since there were positive indications of loss in some of my experiments, and we have instances of its occurrence under more or less analogous conditions in the experiments just cited and in numerous others described in the last article, and since we have in the facts of decomposition and decay, with or without the agency of microbes, as illustrated in the article referred to, a clear explanation of the liberation of nitrogen, there can be hardly any reasonable doubt that such loss did occur in my experiments. But granting such loss, could it have been large enough to materially affect the quantity of nitrogen found at the end, and hence the apparent results of the experiments?

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[1] See Table III of previous article, Expts. 8, 11 and 13.

[2] Ann. Chim. Phys. [5], **22**, 1881, 433.

Neither Boussingault's results nor ours, above cited, give any measure whatever of the loss that may have been induced by like causes in the experiments now under discussion. But, in lack of other data, we may inquire what would be the measure of the effect if the loss here had been the same in quantity as actually occurred in the experiments of Boussingault and in those by Mr. Rockwood and myself.

Taking 15 per cent. of the nitrogen of the seed as the measure of the loss in our experiments, and 45 per cent. of the nitrogen of the nitrates as the measure in Boussingault's, and assuming similar loss in the experiments here under discussion, the influence of each loss upon the main result would be as shown in the last three columns of Table IV.

While it would be absurd to claim that either of the percentages of loss above named is a correct measure of the actual loss in my experiments, and that the figures in either of the last two columns of Table IV are consequently a correct statement of the quantity of nitrogen acquired from the air in any one of these experiments, it is nevertheless clear that if we are willing to allow any such escape of nitrogen here as was actually observed in the analogous experiments of Boussingault, in which the loss was estimated, the effect upon the results would be considerable. If we were to assume, for instance, that the loss was confined to the nitrates in the concentrated solutions and was equal to that observed by Boussingault, we should have in these cases (Nos. 5, 6, 7 and 8), instead of either a small gain or a loss of nitrogen, a gain of from 27 to 57 per cent. while the gain actually observed in the dilute solutions was from 38 to 51 per cent.

TABLE IV.

Acquisition of Nitrogen from Atmosphere by Peas as Actually Observed and as Computed by Allowing for Assumed Loss from Decomposition of either Seed or Nitrates of Nutritive Solution.

Conditions of Experiments.			No. of Experiment.	Gain +, or Loss −, of Nitrogen. In per ct. of Total Nitrogen of Plants.		
				As actually observed in the experiments.	Allowing 15 per ct. of the Nitrogen of the seed to have escap'd	Allowing 45 per ct. of the Nitrogen of the Nitrates of the Nutritive Solutions to have escaped.
				Per cent.	Per cent.	Per cent.
Concentrated Solutions.	Scantily fed.	Smaller nitrogen ration	7	+ 17.2	+ 23.9	+ 34.1
		Larger " "	8	+ 1.5	+ 6.9	+ 32.7
	Well fed.	Smaller " "	5	+ 40.0	+ 43.3	+ 57.1
		Larger " "	6	− 14.0	− 10.5	+ 27.2
Dilute Solutions.	Scantily fed.	Smaller " "	11	+ 38.7	+ 43.9	+ 51.4
		Larger " "	12	+ 38.1	+ 42.1	+ 61.8
	Well fed.	Smaller " "	9	+ 50.0	+ 52.8	+ 64.3
		Larger " "	10	+ 51.1	+ 52.9	+ 73.4

BEARING OF LIBERATION OF NITROGEN UPON THE RESULTS OF OTHER EXPERIMENTS. GAIN OF NITROGEN FROM AIR.

Attention was called by Mr. Rockwood and myself to the lack of uniformity in the outcome of experiments on the escape of nitrogen from seeds and plants during germination and growth. In the experiments of Schultz, in some of those of Lawes, Gilbert and Pugh, and in some of our own, the amounts of nitrogen liberated were very large, though extremely variable; and although in other cases little or no loss was observed, yet the facts now at hand amply confirm the statement of Messrs. Lawes, Gilbert and Pugh that:—

"Taking together the results of all the experiments which have been made [by the authors] upon the decomposition of nitrogenous organic matters, they obviously point to a serious difficulty in the way of experiments made upon the question of the assimilation of free nitrogen by plants. It is not possible to conduct any such experiments without exposing nitrogenous organic matter to conditions more or less analogous to those under which the loss of nitrogen recorded [in the experiments described by the authors] took place. For although, as Boussingault has shown, there may be no loss of nitrogen during germination, yet during the entire period of the growth of a plant, certain portions of the vegetable substance may be subjected to conditions favorable to the decomposition of its nitrogenous compounds and to the evolution of free nitrogen."[1]

Once granting the liability of experiments to this source of error, and considering how entirely unable we are to definitely predict the cases when nitrogen may be liberated, or determine the amount of the loss, it is perfectly easy to see how the results of different experiments on the acquisition of atmospheric nitrogen should be as conflicting as they are.

The remarkably close agreement of duplicate results and of the amounts of nitrogen supplied and found in Boussingault's experiments with plants in confined air or in a current of washed air under glass,[2] would, perhaps, imply that these experiments, in which the nitrogen compounds of the air were excluded in order to test the more accurately the question of the assimilation of free nitrogen, were not materially affected by liberation of nitrogen. Messrs. Lawes, Gilbert and Pugh were also persuaded that there was no considerable escape of nitrogen in their experiments with plants in washed air under glass in which the same question was tested.[3] Possibly plants under such conditions may be less liable to lose their nitrogen than otherwise. But, taking the observed facts together, they seem to imply that abnormal conditions of growth — *e. g.*, insufficient or unfitting nourishment — may be especially conducive to this loss of nitrogen, just as malnutrition of higher organisms renders them less capable of resisting disease.

The early experiments of Boussingault (in 1837–38) with germinating seeds, described in the preceding article, were introductory to others in which the plants were grown for two or three months or more and then analysed. These latter experiments were conducted in the free air of a closed summer-house. The plants, with the exceptions stated in the table herewith, were grown in ignited soil and watered with distilled water. The growth, without food other than that supplied by seed, burnt soil and air, was stunted, but a number of the plants nevertheless attained a respectable size, and put forth buds and blossoms. The principal data and results are given in Table V :

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[1] Phil. Trans. 1862, **2**, 512.

[2] Ann. Chim. Phys. [3], **43**, 149–190.

[3] *Loc. cit.* 514.

TABLE V.

Experiments by Boussingault.—Plants Grown in Free Air of Closed Summer-House.

Kinds of Plants and Times of Experiments.	Quantities of Nitrogen.			Parts of Nitrogen in plants for 100 parts in seed.
	In seed (or plants) at outset.	In plants at end of experime't	Gain +, or Loss —.	
	Mgm.	Mgm.	Mgm.	
Wheat, 1837, 2 months	43	40	— 3	93
Wheat, 1837, 3 “	57	60	+ 3	105
Oats,[1] 1838,	59	53	— 6	90
Clover, 1837, 2 “	110	120	+ 10	109
Clover, 1837, 3 “	114	156	+ 42	137
Clover,[2] 1838,	33	56	+ 23	170
Peas, 1838, 3⅓ “	46	101	+ 55	220
Total : 9 experiments	462	586	+122	132

With the cereals, wheat and oats, the quantities of nitrogen supplied in the seed and found in the plant were about the same, though on the average there was a slight loss of nitrogen. The clover contained at the end of the experiment from 109 to 170 parts, and the peas 220 parts of nitrogen. The excess, barring small errors incident to manipulation, must have come from the air.

The conditions of these experiments were quite similar to those of the experiments of Mr. Rockwood and myself, already referred to, on the germination and growth of peas. The plants in both cases were grown in free air. Boussingault's[1] were in a closed greenhouse. Part of ours were in a greenhouse, part in a dwelling-house, and part out of doors, but protected from rain and dew. Both Boussingault's plants and ours were without nitrogenous food except that supplied by the seed. Boussingault's plants very likely got mineral food from the burnt soil which ours could not get from the washed and ignited sea-sand. This may, perhaps, explain the fact that his plants appear to have been much thriftier than ours. Some of his, indeed, had well-developed seeds. His clover and peas acquired considerable nitrogen from the air in every case, while our peas as uniformly lost nitrogen. It will be remembered that when, in the same series of experiments, he stopped the growth during or near the end of the period of germination, no considerable amount of nitrogen had escaped, while our peas at a nearly corresponding period of development showed a loss of nitrogen. And the gain which Boussingault observed was in accordance with the fact that in my assimilation experiments with peas, the plants receiving food in nutritive solutions and grown in open air out of doors acquired such large quantities of atmospheric nitrogen.

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[1] The plants were started in a field, then taken up June 10, three analysed, and four placed with their roots in distilled water, where they grew and flowered. August 10 they appeared ripe, and were dried and analysed.

[2] The plants were started in ordinary soil, taken up May 28, three analysed and three set out again in purified sand, where they were kept moist with distilled water, and grew, flowering in the middle of July, until August 1st, when they were dried and afterwards analysed.

In the years 1851–54 Boussingault made several series of experiments[2] with haricot beans, lupines, oats, wheat and garden cress, which were grown in ignited sand soil or pumice, fed with ashes of plants or of manure, and moistened with pure water. They were enclosed in a glass case, which was kept in open air out of doors. The case was, however, opened slightly around the bottom and top, so as to allow circulation of air from outside through the case, but to exclude rain and dew. The plants were supplied with the mineral food of the ashes, but no nitrogen except that in the seed and ambient air. The exposure to air was much more limited than if there had been no glass case. The plants were stunted in growth, but had blossoms and, in some cases, ripe seeds. Details and results are summarised in Table VI.

There is here a gain of nitrogen in every experiment but one. Even the cereals, oats and wheat, contain from 17 to 32 per cent. more than was supplied by the seed. The results differ from those of the previous series in that the cereals here show more, and the legumes less, gain of nitrogen. On the whole, there is a smaller gain of nitrogen in this than in the previous series.

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[1] Ann. Chim. Phys. [2] **67**, 5, and **69**, 353.

[2] Ann. Chim. Phys [3] **43**, 1855.

TABLE VI.

Experiments by Boussingault.—Plants Grown in Glass Case with Limited Supply of Air.

Kinds of Plants and Times and Numbers of Experiments.	Quantities of Nitrogen.			Parts of Nitrogen in plants for 100 parts in seed.
	In seed at beginning of expt.	In plants and soil at end of expt.	Gain +, or Loss —.	
	Mgm.	Mgm.	Mgm.	
Dwarf haricot, 1851, '53 and '54, 2½ to 3½ months, 3 expts.	29.3 to 34.9	27.0 to 38.0	—2.3 to + 3.2	92 to 110
Haricot, 1852, 3 months, 1 expt.	21.3	23.8	+ 2.5	112
White lupine, 1853, 3 months, 1 expt.	21.4	25.6	+ 4.2	120
Lupine, 1854, 2¾ and 2 months, 2 expts.	19.9 & 36.7	22.9 & 38.7	+ 3.0 & + 2.0	115 & 105
Oats, 1852, 3½ months, 1 expt.	3.1	4.1	+ 1.0	132
Wheat, 1853, 3½ months, 1 expt.	6.4	7.5	+ 1.1	117
Garden cress,[1] 1854, 2 months, 1 expt.	25.9	27.2	+ 1.3	105
Total in 10 expts.	230.7	249 9	+ 19.2	112

Boussingault suggests that the distilled water which was used for watering the plants of his first series, and which was directly distilled from ordinary river water,[2] may have contained traces of ammonia, which might, perhaps, account for the larger gain of nitrogen in the first series. But it is difficult to see how this could account for the fact that while, in the first series, the legumes acquired relatively large quantities of nitrogen from the air, and the cereals practically none, the cereals in the second series showed a large gain and the legumes sometimes a smaller gain, and in one case a loss.

The differences in the results of similar experiments in the two series just cited are very wide. In a research so remarkable for the care and accuracy manifested in its chemical work as to have since come to be regarded as a classic model in this respect, these discrepancies can hardly be ascribed to errors of analysis, especially when one takes the pains to examine the details of the work. Where the quantities are so small as in the experiments with wheat and oats in 1852–3, such an assumption might be allowable, but in the other cases some other explanation seems called for. A very simple explanation is found in the supposition that nitrogen was liberated in varying quantities in the different experiments.

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[1] 210 seeds were sown; 145 grew, the remaining 65 "acted as manure." That the latter may have lost nitrogen by decomposition would seem by no means improbable. If such was the case, the actual gain of atmospheric nitrogen must have been more than the figures imply.

[2] At the time of the first of Boussingault's experiments the occurrence of minute quantities of ammonia in air and water was not so well understood as it afterwards came to be through his and other researches.

To resume briefly: These experiments of Boussingault, with plants grown in open air the circulation of which was limited and with limited supplies of food, so that the growth was abnormal, gave these two very marked results:

1. Very considerable quantities of nitrogen were obtained from the air. 2. The acquisition of nitrogen, as measured by subtracting the nitrogen supplied from that found at the end of the experiment, was very irregular. Assuming that nitrogen compounds were decomposed and nitrogen set free in varying quantities in the different experiments, as was evidently the case in the numerous instances above discussed, the explanation is very clear. No other so simple and reasonable hypothesis has occurred to me.

Among the well-known experiments on the acquisition of atmospheric nitrogen by plants, are those of Mayer,[1] who has tested the absorption of atmospheric ammonia by the foliage of plants, and concludes that though this is theoretically possible, it probably is so small in extent as to have little or no practical importance.

Excellent as is this research, a careful examination of the details will, I think, warrant the conclusion that the conditions of growth were exactly those which the considerations named above imply to be favorable to the liberation of nitrogen. The plants were, for the most part, very inadequately nourished, that being one of the intended conditions, and were generally stunted and sickly. In cases in which the development was more vigorous, the nutritive solutions were, as the data imply, as concentrated as those in my experiments, in which the escape of nitrogen seems so well established. Here again, therefore, the evidence against the acquisition of nitrogen is seemingly impaired by the abnormal conditions of growth and the, at least possible, escape of nitrogen.

Dietzell concludes, from experiments with peas and clover, that these plants do not assimilate atmospheric nitrogen compounds by their foliage, but here, also, the conditions appear to have been such as to furnish no proof that nitrogen did not escape.[2]

Weiske[3] has reported a series of water-culture experiments with lupines which showed, in a number of cases, a small gain of nitrogen. The plants, however, were stunted and for the most part sickly, and even the healthiest were, in development, "far behind those grown under natural conditions." In one case the plants were cultivated, not in aqueous solution like the rest, but in fragments of filter paper contained in an evaporating dish and kept moist with the nutritive solution, the object being to provide for absorption of nitrogen compounds from the air, and for possible formation of ammonium nitrite by evaporation. In another case the cylinder containing the nutritive solutions was covered tightly, to prevent both absorption of nitrogen compounds and evaporation.

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[1] Landw. Vs. St. **17**, 329.

[2] Landw. Vs. St. **31**, 1884, 166, and Jbt. Ag. Chem. 1884, 297.

[3] Landw. Vs. St. **30**, 1884, 437.

The weight of the plants and the acquisition of nitrogen were both very small where the air was thus excluded, and somewhat larger where the full opportunity was given for access of air and for evaporation. In the last-named case, the one in which the growth of the plants was greatest, the nitrogen in the seed (there was none in the nutritive solution) was 11 mgm. and that in the plant 18 mgm., making a gain of 7 mgm. Weiske infers that nitrogen was acquired from the air, either directly as ammonia, or indirectly by formation of ammonium nitrite through evaporation, but that it came to the plants through the roots rather than the foliage. Considering the abnormal character of the plants, and the small differences between the nitrogen of the seed and that of the plants, the experiments do not seem to me decisive regarding the route through which the atmospheric nitrogen came.

Joulie[1] has lately published accounts of experiments in which there was a large acquisition of nitrogen from the air. The plants were grown in soils contained in glass pots, and kept in open air, but protected from rain and dew. The experiments were conducted through two successive years. In one series buckwheat was grown the first year and ray-grass and hybrid clover the second; in the other, there were no plants the first year and buckwheat the second. In some cases fertilizing materials were used, in others not. The nitrogen supplied and that found at the end of the experiment in plants and soil were compared. Of twenty-two cases cited, two showed a loss and the rest more or less gain of nitrogen. The gain in one case reached 865 mgm. or 577 mgm. per kilo of soil.

The results are very similar to those obtained by myself. Joulie is inclined to ascribe the gain to the fixation of free nitrogen, perhaps by the soil through the agency of micro-organisms, in the manner indicated by Berthelot.

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[1] Compt. Rend. **101**, 1885, 1008.

OTHER CONSIDERATIONS REGARDING THE SOURCES OF PLANT-NITROGEN.

The fact observed in many experiments, that nitrogenous food supplied to the roots of plants, legumes as well as cereals, causes increase of growth, and that the produce, other things being equal, rises and falls with the amount of nitrogen supplied, has been frequently interpreted as indicating that the soil is the only source of the nitrogen of the plants. The field experiments of Messrs. Lawes and Gilbert afford evidence in this direction[1] which, taken by itself, seems very cogent. In these, as the plants are grown year after year on the same land without artificial supply of nitrogen, the yield gradually falls off, and the stock of nitrogen in the soil is at the same time depleted. This is particularly the case with cereals—wheat, barley, etc.—though the same fact is observed with other plants. It is perfectly legitimate to infer that the crops have taken the nitrogen away, and that the succeeding produce is smaller because of this reduction of the supply of mineral food, and especially of nitrogen. The corollary is that the soil is the sole source of the nitrogen.

But we have a closely parallel, though, of course, far less extended, series of results in the experiments cited in Tables I and II above, as may be seen by comparing the "scantily fed" plants with the "well-fed" ones, or the averages with the "smaller" and with the "larger nitrogen rations." The best-fed plants throve best, and when either the total food-supply was diminished or the nitrogen-supply alone was reduced, the mineral food remaining the same, the yield fell off in corresponding degree, as did the amount of nitrogen acquired from the air. Indeed, the uniform parallelism between both the total food-supply and nitrogen-supply on the one hand, and both the total nitrogen in the plants and the amount acquired from the air on the other, was, to myself at least, very surprising.

The phenomenon which is uniformly accompanied by the acquisition of atmospheric nitrogen by the plants in Middletown can hardly prove its non-acquisition by those in Rothamsted. While the Rothamsted plants were taking nitrogen through their roots from the medium in which they grew, and thus reducing the supply of the latter, as was done by the plants in Middletown, may they not also, like the Middletown plants, have acquired some from the air?

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[1] Determination of the Nitrogen in Soils, London edition; and Jour. Chem. Soc. 1885, Trans. 380.

Late experiments by Messrs. Lawes, Gilbert and Warrington[1] lead them to the evidently well-founded and very important conclusion that the leguminous plants somehow favor nitrification, probably through the development of nitrifying ferments, and they are inclined to attribute the peculiar power of the legumes to supply themselves with nitrogen, in part at least, to this function of inducing nitrification of nitrogen compounds previously accumulated in the soil. It is evident, however, that this previously existing store of nitrogen cannot account for all the nitrogen which such plants may acquire, since in my experiments, in which peas were grown in washed and ignited sea-sand, no nitrogen compounds were supplied except the nitrates of the nutritive solution.

Against the acquisition of atmospheric nitrogen by the legumes, Messrs. Lawes and Gilbert cite the observation that clover and other plants of this family, after growing for a number of successive years in experimental fields at Rothamsted, have finally failed, while clover in a garden soil near by, much richer in nitrogen, has continued to do well for a long period of years. The soil in the field has become "clover-sick," a not uncommon experience in Europe, while the richer garden soil has not. In another field the land has become "bean-sick." In other experiments still other leguminous crops have failed after a time. This failure Messrs. Lawes and Gilbert attribute to the depletion of the store of soil-nitrogen, as well that of the lower strata where the clover does a large part of its feeding, as that of the upper strata, a supposition which is strengthened by the fact that the clover continues to grow in the rich garden soil, where the stock of nitrogen is larger. This failure of the clover, beans and other plants to grow continuously for a large number of years may, however, be due to some other cause—for instance, the injurious action of minute organisms, such as have been found by late researches to be a probable cause of the "beet-sickness" in Germany, where land after a time refuses to yield successive crops of sugar beets. If there are organisms

[1] *Loc. cit.*

which thrive upon a specific plant, as the beet, and, when the latter is continuously cultivated, increase until they materially injure it, why may not clover, beans and other plants suffer in like manner? This assumption would accord perfectly with Messrs. Lawes and Gilbert's observation, that the field which has become "bean-sick" is still competent to grow luxuriant crops of red clover, and is, at least, as easy to accept as the hypothesis suggested by Messrs. Lawes and Gilbert, that the success of the one legume after the failure of the other is due to difference of root-habit and root-range.

The Rothamsted field experiments with wheat and barley afford a most striking indication that no considerable quantity of nitrogen is obtained from the air by either these plants or by the soil, in the balance between the income and outgo of nitrogen. Putting on the one side of the account the total nitrogen in the soil, as shown by analysis at the beginning of a long period of years, together with the amount estimated to be brought to the soil by the measurable aqueous deposits, rain, snow, etc., during the same period, and on the other the amounts removed with the crops and with drainage water and the amounts left behind in the soil at the end, the two sides of the account balance with remarkable closeness. The accuracy of this balance implies that the account is correct, and that no other item, such as nitrogen acquired from the air, could be admitted. But this assumes that no considerable loss of nitrogen by decomposition of nitrogenous compounds, such as the facts at hand would lead us at least to regard as possible, can take place, nor does it make any allowance for the acquisition of nitrogen by the soil through the agency of electricity or of micro-organisms, the activity of both of which is indicated by late investigations of Berthelot. On the other hand Messrs. Lawes and Gilbert,[1] Dehérain,[2] Schulz-Lupitz[3] and Heiden,[4] have observed that soils on which leguminous crops had been cultivated for a longer or shorter period have contained more nitrogen than they did before. In the experiments of Lawes and Gilbert, which were with clover, only the surface soil was tested; the first nine inches showed an increase of nitrogen. In Heiden's experiments, observations were made in both surface and subsoil, and the increase of nitrogen in the subsoil during growth of clover after a dressing of lime was very marked. That is to say, while these leguminous plants were acquiring their large quantities of nitrogen, which was to be removed with the crop, the store of nitrogen in the soil was, according to these observations, not depleted, but rather increased. This extremely interesting phase of the general subject demands further study. Meanwhile it is safe to say that the acquisition of atmospheric nitrogen will explain the phenomenon, which otherwise is hardly explicable.

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[1] Am. Jour. Sci. [3] **3**, 28. [2] Ann. Agronom. 1882, 322. [3] Ct. Bt. f. Ag. Chem. 1883, 145.

[4] See von Bretfeld, Das Versuchswesen a. d. Geb. d. Pflanzenphysiologie, 176.

Many familiar facts, such as the often observed facility with which many legumes obtain their large supplies of nitrogen where cereals and other plants fail for lack of it; the thrifty growth of some of these plants in sand, where the soil supply of nitrogen is extremely limited; and the very common refusal of legumes to respond to the application of nitrogenous fertilisers, when the growth of other plants is materially helped by them, all point to a peculiar power of at least some species of plants to provide themselves with nitrogen from natural sources, and are easily understood if we allow that some of their nitrogen comes directly from the air; while, if this assumption is denied, the facts can hardly be explained.

Two different ways by which the free nitrogen of the air may be made available to plants have been suggested by late researches of Berthelot. One is the fixation of nitrogen by vegetable matters through the agency of electricity.[1] The acquisition of nitrogen by living plants through this means will doubtless be best discussed after the publication of further results which Berthelot has promised. The other is the no less remarkable observation that soils containing clay may fix large quantities of free nitrogen through the aid of living organisms,[2] which may perhaps give us an explanation of the increase of nitrogen in the soils on which leguminous plants have been grown by Lawes and Gilbert, Dehérain, Schulz-Lupitz and Heiden. I do not see how they can explain the acquisition of nitrogen in my own experiments, however. It would seem that if the fixation of nitrogen in my experiments was due to the agency of microbes, the plants themselves must have had a share in the operation, since neither purified sand alone, nor an aqueous solution of salts, nor both together, so far as I am aware, have ever been shown to have any power of gathering nitrogen, except in so far as solutions may take nitrogen compounds from the air.

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[1] Ann. Chim. Phys. **10**, 52, and **12**, 457.

[2] Compt. Rend. **101**, 775.

In brief, strong as is the evidence which comes from the greenhouse and the field in support of the view that neither the legumes nor any other plants acquire any material amount of nitrogen from the ambient air—and, leaving loss of nitrogen by decomposition out of account, this evidence is extremely cogent—it nevertheless fails to explain some of the most important of the observed facts of production, and is circumstantial and cumulative rather than positive and absolute, and hence cannot avail against absolute testimony on the other side.

The considerations above urged regarding the liberation of nitrogen seem to me to help greatly toward explaining the negative results that have been so often obtained. Positive evidence of the acquisition of atmospheric nitrogen by plants is furnished not only by my own experiments, but by those of Joulie and others in the greenhouse and laboratory, and is reinforced not only by the testimony found in the field by Lawes and Gilbert, Dehérain, Schulz-Lupitz and Heiden, but also, though with less definiteness, by the facts of common observation.

CONCLUSION.

The considerations above presented may be summarised as follows:

1. The experiments in which peas were grown in open air, as detailed in a former, and recapitulated in the beginning of this article, showed in some cases a large acquisition of nitrogen from the air, the gain amounting in some instances to half or more than half of the whole nitrogen in the plants. In other cases there was, apparently, a very small gain or a loss of nitrogen. There seems to be excellent ground for assuming that the cases in which either only a small gain or a loss of nitrogen was observed (in all of which the conditions of growth were abnormal) are to be explained by the escape of nitrogen from either the nitrates of the nutritive solution or from the seeds during germination, or from the growing plants. The proof of the acquisition of atmospheric nitrogen which is furnished by the cases in which the conditions of growth were normal, in each of which the amount acquired was large, is thus rendered the more emphatic.

2. That plants grown in open air may acquire nitrogen from the air was long ago observed by Boussingault. His plants, however, received no nitrogen except that from the seed, and the quantities of atmospheric nitrogen acquired were small. The fact that so much more was obtained in my experiments, in which the plants were liberally supplied with food, may be explained by either of two very plausible hypotheses. The plants grown under normal conditions may have been in better condition to resist the action of denitrifying ferments or other agencies which would set nitrogen free, or they may have been better able to assimilate nitrogen from the air. Of course these hypotheses need further proof before they can be entitled to unqualified acceptance. The lately published experiments of Weiske, and especially those of Joulie, afford still further corroboration of the acquisition of nitrogen from the air.

3. Numerous other experiments have shown very slight gain or more or less loss of nitrogen, so that the evidence at hand, taken altogether, is quite conflicting. The liberation of nitrogen from the germinating seeds, as well as from the nitrogenous food supplied, affords a simple and, to say the least, not unreasonable explanation of much of the discrepancy. That there is liability to such loss, at times very considerable, is certain. Tending, as it does, to reduce the quantity of nitrogen found at the end of the experiment, and hence the quantity apparently acquired from the air, it is easy to see how there might really be a considerable gain of nitrogen from the air in an experiment in which the comparison of the nitrogen supplied with that found at the end implied only a small gain or even a loss. The failure of an experiment to show the acquisition of nitrogen from the air proves the non-assimilation of atmospheric nitrogen only on condition of the further proof that no nitrogen was liberated, while a gain actually observed is positive proof that the nitrogen is assimilated either directly by the plants or indirectly through the medium in which the roots developed.

4. The liberation of nitrogen appears to be due, in some cases, if not in all, to ferments. To explain why it should take place in one case and not in another, is as difficult as to account for the fact that zymotic diseases attack one animal and not another, or that the potatoes of certain fields or some of the apples in a barrel are struck with decay, while others escape. It is, however, notice-

able that in nearly all the experiments in which no gain of nitrogen has been observed the plants have been ill fed, or the nutritive solutions have been very concentrated, or other conditions have been abnormal; while, so far as the details at hand show, the largest gains have been found in the cases where the conditions of growth were most favorable. This accords with the common observation that organisms weakened by insufficient nourishment or otherwise are generally less able than those in normal condition to resist zymotic diseases.

5. How the nitrogen was obtained in the experiments in which its acquisition is proven is still a matter of doubt. It must have been taken as either free or as combined nitrogen, and either directly through the foliage or indirectly through the soil and nutritive solutions and the roots of the plants.

6. It would be going too far to positively assume that in the experiments which have given the strongest evidence against the fixation of free nitrogen by plants—namely, those of Boussingault and of Lawes, Gilbert and Pugh, in which the plants were raised under glass, in confined air or in air washed free from nitrogen compounds—the negative results are due to escape of nitrogen in the manner above suggested, though such liberation cannot be regarded as impossible. But it is at least conceivable that the measures adopted to exclude nitrogen compounds—keeping the plants under glass and passing the air through acid and alkali solutions before entering—may have excluded the action of electricity or of microbes, by which the fixation of free nitrogen may perhaps be effected. The plants were also, for the most part, very poorly fed. That this may be the cause of deficient assimilation of nitrogen is indicated by the experiments with peas above referred to. At any rate, until we know more about the relations of electricity and of micro-organisms to the fixation of nitrogen, we can hardly be warranted in assuming that these experiments prove that plants grown under normal conditions do not assimilate the free nitrogen of the air.

The fact that the observed cases of large acquisition have been with plants in open air, might be taken as indicating that the ammonia and other nitrogen compounds of the atmosphere are the source of the nitrogen obtained, were it not that the amounts acquired have, in some cases, been several times as large as the apparently possible maximum.[1]

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[1] This Journal **6**, 376–381.

7. To what extent the attested acquisition of atmospheric nitrogen is a function of the plant alone; in how far it may be dependent upon the action of electricity, microbes, or other agency induced by the plant; by what species of plants and under what conditions it is accomplished, are of course matters for further study. The experiments of Berthelot imply that organic matter, through the agency of electricity, and soils containing clay, through the agency of living organisms, may fix the free nitrogen of the air. It may hence be inferred that in some of the experiments in which acquisition has been observed, the nitrogen may have been first taken from the air by the medium in which the roots grew and communicated through the latter to the plants. But in my experiments this medium consisted of ignited sea-sand and an aqueous solution of salts. I am aware of no observed facts to imply that these, separately or together, are able to fix free nitrogen by aid of electricity, micro-organisms, or any other means. In the present state of our knowledge, therefore, the balance of probability seems to decidedly favor the assumption that the plants themselves must be factors in the acquisition of atmospheric nitrogen.

8. Messrs. Lawes, Gilbert and Warrington have shown the great probability that the legumes, which appear to possess in high degree the power of obtaining nitrogen from natural sources, induce the action of nitrifying ferments by which the inert nitrogen of the soil is made available. It is equally conceivable that the same plants and others may favor the action of nitrogen-fixing micro-organisms.

To recapitulate in few words: The experimental testimony regarding the acquisition of atmospheric nitrogen by plants is conflicting. But the evidence against it which comes from the laboratory and the greenhouse is based upon experiments whose conditions were more or less abnormal in respect to food-supply or access of nitrogen compounds or otherwise. In those which seem most conclusive against the assimilation of free nitrogen the arrangements were such as may have hindered the action of electricity, if not that of nitrogen-fixing micro-organisms, two agencies toward which late research points as possible, if not certain, factors in the fixation of nitrogen. In all there is the possibility, and in some a very strong probability, that the results may have been affected by liberation of nitrogen from seeds or plants or food supplied, a liberation which is sometimes, if not always, due to ferments. This may materially reduce the nitrogen found at the end of the experiments, and with it the apparent gain of nitrogen from the air. The evidence from the field against the assimilation is of necessity more or less incomplete, since, to say nothing of other difficulties, some of the important factors of the problem, such as the acquisition of nitrogen by the soil and its liberation from the soil, are inadequately settled or left entirely out of account. And, finally, to deny the acquisition of atmospheric nitrogen is to leave some of the most evident facts of production unexplained.

On the other hand, the evidence in favor of the acquisition of nitrogen by plants, legumes especially, from the atmosphere during their period of growth is direct and positive. In pot experiments the gain has been at times very large, and in comparative trials it has been larger or smaller in proportion as the conditions have been more or less nearly normal. Less accurate, but at the same time very strong, evidence in the same direction comes from experiments in the field. The conclusion that plants acquire atmospheric nitrogen accords with and explains facts of vegetable production otherwise unexplained. And late research leads us to hope that the explanation of the processes by which the nitrogen is acquired may be found, perhaps, in the near future.

It is reasonably certain that the combined nitrogen of the atmosphere is assimilated by plants. If the results of research should continue to develop in the same direction in which they have been developing of late, it will require but a short time to place the assimilation of free nitrogen beyond question. Unless future research should bring evidence directly opposed to the best now at hand, it must be allowed that the greater part of the nitrogen which the plants obtain from the air comes through the foliage. The faculty of obtaining nitrogen from the air appears to be especially characteristic of the legumes. By what species of legumes or other families of plants it is possessed, it is as yet impossible to say.

But, whatever may be the plants that acquire atmospheric nitrogen, the ways by which they acquire it or the form in which it comes, the fact of its acquisition in considerable quantities seems well established.

MIDDLETOWN, CONN., *July* 1, 1886.

THE INDIRECT ESTIMATION OF CHLORINE, BROMINE AND IODINE BY THE ELECTROLYSIS OF THEIR SILVER SALTS.

WITH EXPERIMENTS ON THE CONVERTIBILITY OF THE SILVER SALTS BY THE ACTION OF ALKALINE HALOIDS.

BY J. EDWARD WHITFIELD.

In the absence of reliable methods for the direct quantitative separation of bromine and chlorine, it is usual to employ one or other of the methods for the conversion of the mixed silver salts to a common condition.

Both the reduction to silver by hydrogen and the conversion of the bromide to chloride by heating in an atmosphere of chlorine are attended with loss by volatilisation and mechanical transfer, and the possible inaccuracy of both the processes is such that they can scarcely be considered as available for the estimation of small amounts of either constituent in presence of large amounts of the other.

Of all such methods the electrolytic analysis of the mixed and fused silver salts, as proposed by Bolley,[1] and more recently introduced and tested by Kinnicutt,[2] is probably the best, though, according to Finkener,[3] perfect decomposition is difficult to obtain by this method, and there is danger of volatilisation and partial change of the silver salts in the fusion.

Kinnicutt's test analyses of the fused salts show, for silver chloride and silver bromide each by itself, errors of 0.0006 gram — to 0.0003 gram + on amounts varying from 0.7 gram to 1.8 grams; and for the mixed silver chloride and bromide, errors from 0.0010 gram — to 0.0012 gram +, with a mean of 0.0006 gram + on weights varying from 2 grams to 2.8 grams.

These figures represent the sum of the errors from the weighing of the fused chloride to the weighing of the deposit of silver, and do not include errors made in the precipitation, filtration, transfer to crucible and fusion.

A method in which the decomposition of the silver salts may be effected without fusion, and which would at the same time place the errors of filtration, preparation for weighing and subsequent electrolysis at a minimum, seems to be desirable, and a promising line of investigation was suggested by Luckow's assertion[1] that from the solution of silver chloride in potassium cyanide the silver may be thrown down completely.

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[1] Dingl. Pol. Jour. **151**, 46. [2] This Journal **4**, 22. [3] Rose-Finkener, Quant. Anal. **2**, 621.

Luckow gives no figures excepting a common mean of all determinations by the precipitation from the cyanide solution and the decomposition of the solid chloride on the negative pole of the battery under sulphuric acid, so that the first experiments were made to test the accuracy of the battery process under these conditions.

In experiments (1)–(5) silver chloride was the starting-point. In (1)–(3) the freshly precipitated and carefully washed chloride was dried to a constant weight in a platinum dish, protected from the light, at a temperature of about 150° C., dissolved in potassium cyanide, and electrolysed after the addition of a little sodic hydrate, preliminary analyses having seemed to indicate that the presence of sodic hydrate affected the deposition favorably. In all subsequent experiments ammonia, which was found to be of equal service, was used instead of sodic hydrate.

In experiments (4) and (5) the chloride was converted, previous to electrolysis, into the bromide by solution in potassium cyanide, the addition of potassium bromide and precipitation by sulphuric acid as will be described later, and the precipitate redissolved in potassium cyanide, the object being to test the action of the battery upon the cyanide solution of the silver bromide.

	AgCl taken.	Silver found.	Silver calculated.	Error.
(1)	0.1565 gram.	0.1177 gram.	0.1178 gram.	0.0001 gram —
(2)	1.3004	0.9785	0.9787	0.0002 —
(3)	2.2657	1.7047	1.7051	0.0004 —
(4)	0.7472	0.5618	0.5624	0.0006 —
(5)	0.2854	0.2133	0.2147	0.0014 —

These results, as far as they go, are satisfactory. Similar tests upon the electrolysis of silver bromide and silver iodide in the cyanide solution were undertaken, but it was thought advisable to combine, incidentally with the tests of the battery process, an examination of the method recently proposed by Maxwell-Lyte[2] for the direct conversion of silver chloride to the bromide and thence to the iodide.

Field[3] was the first to propose a quantitative conversion of silver chloride to the bromide by digesting the former in potassium bromide, and the change of the chloride or bromide to the iodide by the action of potassium iodide upon these salts. This method has been variously criticised and finally abandoned as an accurate process,[1] though, so far as concerns the conversion of the chloride and bromide to the iodide, Siewert[2] shows it to be exact.

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[1] Dingl. Pol, Jour. **178**, 43.

[2] Chem. News **49**, 3.

[3] Jour. Chem. Soc. 10, 234.

Maxwell-Lyte's method of proceeding, depending upon identically the same principle which Field attempts to utilise, consists in the solution of the silver haloid salts in potassium cyanide, the addition of potassium bromide, the decomposition of the potassium cyanide by means of sulphuric acid, with the consequent precipitation, and weighing of the silver bromide mixed with the iodide of the original mixture—the resolution of this precipitate in potassium cyanide, the addition of potassium iodide, the decomposition of the cyanide as before, with sulphuric acid, with the formation of a precipitate which is presumably pure silver iodide and to be weighed as such.

To convert the chloride to the bromide Maxwell-Lyte uses a weight of potassium bromide equal to the weight of the silver chloride taken; and to change the bromide to the iodide, a weight of potassium iodide one and a quarter times as great as the original weight of the silver chloride.

In the following experiments these amounts have varied widely, but the proportions of alkaline haloid salts employed are given for each case in the tabular statement.

The starting-point was generally freshly precipitated silver chloride, but in the last three cases, pure silver, this being dissolved in nitric acid, precipitated with potassium bromide (two equivalents), and the precipitate dissolved in potassium cyanide, converted into the iodide in the manner described, and weighed, the object of this being to test the convertibility of the silver bromide to silver iodide.

In most cases the final precipitate, after weighing, was electrolysed, so as to have a more perfect control upon the results of the conversion process, and at the same time to test the battery method additionally.

The bromide and iodide of silver were precipitated hot from dilute solutions, which were cooled and allowed to stand over night to settle before filtering.

Filtrations were made by the use of the Gooch crucible, with gentle pressure; the silver salts were dried directly over a low Bunsen flame at a temperature far below the melting-point, and dissolved, after weighing, by introducing crucible and asbestos into a strong solution of potassium cyanide, and heating, the time necessary for the solution varying from a few minutes to several hours, according to circumstances.

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[1] Rose-Finkener, *loc. cit.*

[2] Zeit. für anal. Chem 7, 469.

In some cases traces of reduced silver were found with the asbestos, and were recovered by treating the felt with nitric acid and washing, the filtrate and washings being added to the main solution.

The deposition of silver was made in the platinum dish of 100 $cm.^3$ capacity, which held the solution, and the current found most suitable was (as Luckow originally recommended[1]) developed by four Meidinger cells of large size.

With solutions of the volume named and the area of the negative electrode employed, it was found advisable not to attempt to treat more than two grams of the silver salt.

The solution was decanted immediately on the stopping of the current, or better, syphoned off while the battery connections were still unbroken, and washed with distilled water, to prevent the solvent action of the cyanide on the deposit.

	AgCl taken.	AgBr found.	AgBr calculated.	Error.	Equivalents of KBr taken.
(6)	0.3260 gram.	0.4227 gram.	0.4270 gram.	0.0043 gram —	2
(7)	0.3093	0.4023	0.4052	0.0029 —	2
(8)	1.3801	1.8041	1.8080	0.0039 —	2
(9)	0.2091	0.2723	0.2739	0.0016 —	10
(10)	0.6846	0.8909	0.8968	0.0059 —	10
(11)	1.1625	1.5202	1.5230	0.0028 —	20
(12)	1.1734	1.5310	1.5372	0.0062 —	20
(13)	0.3501	0.4553	0.4586	0.0033 —	29
(14)	0.4178	0.5468	0.5473	0.0005 —	29

	AgCl taken.	Silver found.	Silver calculated.	Error.
(6)	0.3260 gram.	0.2443 gram.	0.2453 gram.	0.0010 gram —
(7)	0.3093	......	......	......
(8)	1.3801	1.0385	1.0386	0.0001 —
(9)	0.2091	......	......	......
(10)	0.6846	0.5137	0.5152	0.0015 —
(11)	1.1625	......	......	......
(12)	1.1734	0.8829	0.8831	0.0002 —
(13)	0.3501	0.2634	0.2634	0.0000
(14)	0.4178	......	......	......

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[1] *Loc. cit.*

	AgCl taken.	AgI found.	AgI calculated.	Error.		Equivalents taken of KI.
(15)	0.6996 gram.	1.1451 gram.	1.1456 gram.	0.0005 gram	—	2
(16)	0.7587	1.2429	1.2424	0.0005	+	2
(17)	0.6710	1.0992	1.0988	0.0004	+	10
(18)	0.2515	0.4118	0.4118	0.0000		10
(19)	0.6501	1.0646	1.0646	0.0000		10

	AgCl taken.	Silver found.	Silver calculated.	Error.	
(15)	0.6996 gram.	0.5255 gram.	0.5265 gram.	0.0010 gram	—
(16)	0.7587	0.5691	0.5710	0.0019	—
(17)	0.6710	0.5042	0.5050	0.0008	—
(18)	0.2515	0.1892	0.1892	0.0000	
(19)	0.6501	0.4892	0.4892	0.0000	

	Silver taken. gram.	AgI found. gram.	AgI calculated. gram.	Error. gram.	Equivalents taken of KI.	Silver found. gram.	Error. gram.
(20)	0.5418	1.1790	1.1789	0.0001 +	2	0.5417	0.0001 —
(21)	0.3750	0.8154	0.8159	0.0005 —	2	0.3746	0.0004 —
(22)	0.4078	0.8859	0.8873	0.0012 —	10	0.4077	0.0001 —

From these experiments it appears that the deposition of silver from the cyanide solution of the chloride, bromide or iodide is exceptionally exact; the tendency of the process, however, is to yield low results, and yet, in spite of the multiplicity of operations through which the original material has been passed in the attempt to settle two questions at once, the deficiency is not very great, being 0.0005 gram in the mean of eighteen determinations, with a maximum value of 0.0019 gram.

The conversion of silver chloride to silver bromide by the method proposed by Maxwell-Lyte is, like its predecessor, too imperfect to be worthy of trust; but the experiments indicate unmistakably that the change of silver chloride or silver bromide to silver iodide is sufficiently complete to afford the basis of a good analytical method.

The indirect estimation of chlorine and bromine, chlorine and iodine, or bromine and iodine, in presence of one another, may be effected satisfactorily, therefore, by precipitating both together as silver salts, filtering on asbestos, washing, drying at 150° C., weighing, dissolving the residue in potassium cyanide, and either electrolysing the solution to determine the silver or precipitating the silver as iodide, again filtering upon asbestos, washing, drying and weighing.

In a mixture of all these halogens the iodine is first to be separated by known methods and the chlorine and bromine indirectly estimated as described.

Laboratory of U. S. Geological Survey, Washington, D. C., *June*, 1886.

NOTES OF WORK FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF VIRGINIA.

No. XV.

Communicated by F. P. DUNNINGTON.

127.—ON MERCUROUS HYDRATE.

BY G. B. BIRD.

Since cupric hydrate is readily formed by precipitation, at common temperatures, with an alkaline hydrate, and is subsequently so easily decomposed by heat, it appeared probable that, while the oxides of silver and mercury are precipitated from their solutions by alkaline hydrates, the corresponding hydrates of these would be formed if operating at a lower temperature. Pursuing this suggestion, in this laboratory, in 1884, Mr. J. D. Bruce undertook the formation of argentic hydrate; and it appeared that in dilute alcohol argentic hydrate decomposes at all temperatures above —40° C.[1] Employing a similar method, Mr. Bird has endeavored to obtain mercurous hydrate.

A dilute solution of mercurous nitrate was mixed with alcohol, cooled to — 18° C., and the small amount of salt which separated filtered off, thus obtaining 70 per cent. alcohol saturated with mercurous nitrate. A similar solution of potassium hydrate was made, and in the following experiments these were used in such amounts as gave a slight excess of the potassium hydrate solution.

When mixed at common temperature these alcoholic solutions afforded the same brownish-black precipitate of mercurous oxide that is obtained from aqueous solutions. Corresponding portions of these solutions were put into test tubes and these cooled to — 37° C. and then united and mixed by stirring; a flocculent precipitate of red-amber color was slowly formed, which subsided very slowly; as this was warmed, it gradually darkened, until at — 18° C. it was of a slate-gray color, with a yellowish-green portion suspended in the liquid.

Another experiment, beginning at a temperature of — 39° C., afforded the same results.

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[1] Chemical News, No. 1301, 208.

The most satisfactory experiment was made on a morning when the temperature of the atmosphere was — 18° C.

The bottom of a test tube was perforated and the tube was then drawn out, forming a pipette, the bulb of which was at its lower end, and fitted into another test tube, in which the potassium hydrate solution was put; by this arrangement the solution could be cooled in the pipette and transferred to the tube containing the mercurous nitrate with very little alteration of temperature. Using sufficient of one solution to correspond to one pipetteful of the other, these were cooled to —42° C. The perfectly clear though somewhat viscous liquids were then mixed. At first the solution showed only a pale yellow color; after a minute a very pale amber flocculent precipitate formed slowly and remained suspended in the liquid; after two hours the temperature had risen to —23°C., the main portion of the precipitate had subsided and was darkened a little, the suspended portion being yellowish-green; after four hours the temperature was — 18° C. and the precipitate of a dirty yellow color; after six hours the temperature was — 10° C., the color was slightly darker and more greenish. A portion of this precipitate was collected, dissolved in cold nitric acid, and proved to contain much mercuric salt.

Judging from the colors of the corresponding compounds of lead, copper, silver and mercury, it appears very probable that the pale-amber-colored precipitate obtained was mercurous hydrate, and that it readily decomposes by heat, forming, in part, mercurous oxide and water, and more largely, mercuric oxide, mercury and water.

128.—EXAMINATION OF A SUPPOSED METALLIC METEORITE FROM HIGHLAND COUNTY, VIRGINIA.

By F. P. Miles.

This specimen was received from J. K. Campbell, Esq., of Monterey, Va. It weighs about 1.5 kilograms, and is approximately a flattened oval mass of which the greatest dimensions, taken at right angles, are 15 × 10 × 3 cm., and thinning toward the edges. Upon one edge there is firmly imbedded a small piece of white sandstone, and the compact mass of iron is covered with a thin film of rust. The sp. gr. of the mass = 6 34. An analysis of a bright, clean piece of the metal gave—

Iron,	99.716
Phosphorus,	.106
Carbon,	.032
Sulphur,	.058
	99.912

Nickel and cobalt were carefully tested for, but were not present. It appears quite certain that this specimen is of terrestrial and artificial origin, and was probably produced in one of the early "bloomery" fires, from the fossil ores lying in the Clinton beds, which are largely exposed in that neighborhood; although there is no record or tradition of any such furnace in this portion of the county.

129.—ON THE FORMATION OF PLATINUM SILICIDE.

By F. P. Miles.

In an article from this laboratory, communicated by Professor W. G. Brown,[1] there is given an account of a formation of platinum silicide. A platinum crucible containing powdered topaz was placed within a graphite crucible, between these a layer of Jennings' calcined magnesia[2] was packed, and the top of the crucible luted on with clay. After heating the crucible thus charged, the platinum silicide was found within. I then proposed to search for the essential conditions of this result, and Mr. Miles has carried out the following experiments:

A supply of carbon monoxide was collected in a gas-holder and dried by sulphuric acid as used. This was passed to the bottom of a glass flask in which silicon fluoride (with some hydrofluoric acid) was generated, and thence through a glass tube which terminated in a platinum tube, made by rolling up a piece of foil and fusing the end of the glass tube to it.

The following results shed some light upon the point in question:

The flame from a hot-blast burner fed with oxygen was directed upon the platinum tube; the latter was soon perforated, the edges of the hole being well rounded and malleable. In the subsequent experiments, air was substituted for oxygen, and the hottest flame then attainable was insuffiicent to fuse the empty metal tube.

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[1] This Journal, 7, 172.

[2] Containing a trace of Na_2SO_4.

The silicon fluoride alone, and with carbon monoxide, was passed through the heated tube, but the metal was unaltered.

Then a little Jennings' magnesia was put inside the tube and each of these gases passed through the heated tube, with the same result. Finally the mixture of silicon fluoride and carbon monoxide was passed over the magnesia and heated, with the following results: At a bright red heat the platinum was perforated and the edge of the metal was thickened on the side next to the magnesia, forming a small amount of a mass which resembled, as far as it could be examined, the platinum silicide above referred to. It was crystalline, brittle, hardness about 4.5, fusible on charcoal before the blowpipe, and when treated with aqua regia dissolved slowly, with separation of small particles of silica.

It appears, therefore, that at the temperature employed, the decomposition of the silicon fluoride is dependent upon the presence of both the reducing gas carbon monoxide and the strongly basic element magnesium to combine with the fluorine, in order that the platinum silicide shall be formed.

130.—ANALYSIS OF A COPPER SLAG OF BRIGHT RED COLOR.

By N. A. Berry.

This slag was obtained from the Canton Copper Works, Baltimore, Md., where it is occasionally produced in the process of refining copper.

It is very tenacious and hard, breaks with conchoidal fracture and knife-like, splintery edges, having scattered throughout its mass small spherical cavities and also very minute metallic beads; is opaque, and its color varies from bright to darker scarlet. Sp. gr. = 2.987; H = nearly 6. When reduced to powder and treated with hydrochloric and nitric acids there remained, together with silica, a pale yellow powder; this portion was fused with soda and analysed separately. The following was found present:

		Molec. ratio.
Soluble in acids:		
Copper,	2.50	
Cuprous oxide,	27.05	18.95
Ferrous oxide,	.25	.34
Alumina,	.43	.42
Insoluble in acids:		
Cuprous oxide,	8.64	6.05
Ferrous oxide,	11.69	16.24
Silica,	49.24	82.07
	99.80	

From the oxygen ratio for bases and silica, 1:4, it appears that cuprous oxide can combine with a surplus of silica as do the alkalies in petalite or orthoclase.[1] It is also of interest to note the *pale yellow* color of the insoluble silicate, which contains so large a per cent. of iron and copper, probably presenting the effect of mixture of the complementary colors, green and red, which would belong respectively to the simple ferrous and cuprous silicates. No doubt this slag is familiar to all copper smelters; but, since I have not been able to find it mentioned in any treatise on metallurgy, its composition may prove of interest.

131.—COMPOSITION OF MIRROR AMALGAM.

By Gessner Harrison.

In Watts's Dictionary of Chemistry[2] we find described tin amalgams having the formulæ Hg_2Sn, $HgSn$, Hg_2Sn_3, but there is no mention of the composition of the very familiar amalgam employed in making mirrors, nor do I find such in other chemical works.

A specimen of "first-class German" mirror was taken, the amalgam, well cleansed with alcohol and water, was removed and dried over sulphuric acid; its analysis afforded the following:

		Atomic ratio.
Tin, ...	83.78	8.55
Mercury, ...	16.60	1.

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[1] Amer. J. Sc. **44**, 398, 1867.

[2] **3**, 890.

Giving approximately the formula Hg_2Sn_{17}, since in the manufacture of mirrors the excess of mercury is removed from the amalgam uniformly by pressure, it follows that there will be some little variation in the amount of mercury remaining. In view of the definite compounds which may be obtained containing a larger proportion of mercury, this presents an illustration of the decomposition of a compound by pressure.

132.—ANALYSIS OF "PURE ZINC" MADE BY THE BERTHA ZINC COMPANY, PULASKI COUNTY, VA.

By G. B. Bird.

The above-mentioned company manufactures from ore, essentially calamine, an excellent grade of zinc, which afforded on analysis (by F. P. D. in 1881) the following:

Lead,	.0500
Silicon,	.0168
Iron,	.0140
Carbon,	.0580
Arsenic,	.0001
Sulphur,	...
Zinc, by diff.,	99.8611

Through the kindness of Mr. Thos. Jones, Superintendent, a portion of the commercial spelter was charged into one of the upper retorts of the furnace and redistilled at a less heat. Analysis of which gave:

Lead,	.0225
Silicon,	.0019
Iron,	.0121
Carbon,	none
Arsenic,	none
Sulphur,	.0006
Zinc, by diff.,	99.9629

It therefore appears that while other impurities are largely removed, the small amount of iron is scarcely diminished by redistillation from a fire-clay retort with iron front, such as is usually employed in the Belgian process. This metal answers excellently for most of the laboratory processes in which zinc of high degree of purity is demanded.

133.—ANALYSIS OF SHOT.

By H. Hardaway.

Seeing that the statements made as to the amount of arsenic in the lead employed for making shot are not very definite, and are apparently not based upon any recent analyses, it appeared of interest to ascertain whether or not there is so much variation in the composition of this alloy as now made. From the brands in our market the following were selected, all being clean, well-shaped bird-shot :

No. 1.—Wythe Lead and Zinc Mine Co., Virginia.
No. 2.—Merchants' Shot Tower, Baltimore.
No. 3.—Leroy Shot and Lead Manufacturing Co., New York.
No. 4.—Fatham Bros., New York.

A complete analysis of each of these was made, employing for each over 100 grams, from which the lead was separated as sulphate, but estimated by difference, affording the following results :

	No. 1.	No. 2.	No. 3.	No. 4.
Arsenic, . . .	.0824	.0393	.2725	.1413
Iron, . . .	.0986	.0167	.0099	.0121
Copper, . . .	.0072	trace	.0081	.0107
Silicon, . . .	.0041	.0050	.0002	.0023
Carbon, . . .	.0115	.0269	.0041	.0055
Lead, . . .	99.7962	99.9121	99.7052	99.8281

We find in Muspratt's *Chemistry*,[1] as to the amount of arsenic present: "The limits are from 3 to 8 or 10 parts in 1000, the lesser quantity being employed, as the lead is more ductile and the larger when it is hard." In this selection of American shot it is seen that the amount is much smaller, and the range yet wider, being from .4 to 3.0 parts in 1000. It does not appear from these results that there is any special connection between the amount of arsenic and copper and iron, yet it is to be noted that the amount of arsenic increases as that of silicon diminishes.

University of Virginia, *Sept.*, 1886.

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[1] 2, 474.

PEPSIN *VS.* ANIMAL DIGESTION.

By E. F. Ladd.

In a previous number of this Journal[1] I gave the result of trials in the artificial digestion of the albuminoids of our feeding-stuffs; in this I propose to give data showing the reliability of the method, and the close correspondence of results to those of the German trials for similar feeds, and to the few experiments made by American investigators in animal digestion.

From Kuhn's[2] tables of digestibility I give the column of averages for all substances similar to those of my own trials. While his are, in many cases, the average for several trials showing a wide range of digestibility, my own, only trials in duplicate of a single sample. Had I made more determinations, using different samples, no doubt the differences between our coefficients would be even less than they now are.

Per Cent. Albuminoids Digested.

	Pepsin method.	Kuhn's German tables.
Red clover, ...	65	67
Clover hay, ...	74	70
Lucerne, ...	78	77
Sorghum, ...	58	56
Wheat straw, ...	25	26
Pea meal, ...	88	88
Oat meal, ...	82	87
Bean meal, ...	95	90
Cotton-seed meal, ...	89	87
Wheat bran, ...	83	88
Wheat bran, ...	70	70
Linseed meal, ...	89	87
Corn meal, ...	72	78 to 85
Average for the above, . . .	74.46	74.69

So far as results obtained on similar feeds can test the reliability of a method, the proof given in the above tabulated parallels is sufficient to show the method to be worthy of further consideration. I also had a chance to make a trial with a small sample from the same material used in two of the digestion experiments at the New York Experiment Station.[1] A small sample of the *Soja hispida* bean fodder, also of the corn fodder used in these experiments, that had been taken for analysis, remained on hand when I began my experiments in pepsin digestion. These I tested, with results as follows below:

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[1] 8, No. I.

[2] Armsby's Manual of Cattle Feeding.

	Corn fodder.	Soja fodder.
Pepsin digestion, . . .	54	75
Animal digestion, . . .	49	70

Had I made trials with samples taken each day of the digestion experiment, or a single trial of all the samples mixed, the small difference between the digestion coefficients for the animal and pepsin method might have been even less. I say small difference, for small it is as determined in nitrogen, the five per cent. difference in the soja fodder representing but one-tenth of one per cent. of nitrogen; according to Armsby,[2] but little more than the probable error for a single determination in fodder analysis for the nitrogen, and less than the probable error in animal digestion.

Assuming that the animals used in the above-named experiments were of normal digestive powers, and granting that the assumed digestibility from the German tables of the grain fed was really the actual digestibility, and omitting for the time the probable influence on digestion of compounded rations, we still have a close approximation of results.

In the light of evidence obtained since that date, there seems good reason for doubting the applicability of the digestion coefficient for the corn meal in this particular instance, as assumed from the German tables. My own experiments show that with our flint corns the digestion coefficient is considerably less than that given in the German tables. The few trials made with dent or soft corns lead me to think their albuminoids have a higher digestion coefficient than the flints. It may be that the German experiments were made with dent corn, thus reconciling the difference. If this be true, then there would be little or no difference in the results between the animal and pepsin digestion in the above trials.

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[1] Third Annual Report for 1884.

[2] Wis. Exp. Station Report, 1886, 137.

I give further, for comparison, single trials made by different investigators in comparison with my own—a sample of cotton-seed meal by Armsby;[1] also four hays by Wolf.[2]

	Pepsin digestion.	Animal digestion.
Cotton-seed meal,	88	89
Lucerne,	74	75
Red clover,	65	60
Red clover,	65	57
Meadow hay,	57	58

Armsby[3] and others have pointed out that the relative quantity of the several nutrients in a fodder has an influence on the digestibility. "Thus, if a fodder be made over rich in starch, the digestibility of the albuminoids is decreased." This we find to be the case in artificial digestion.

	Per cent. digested.
Corn meal,	70
Corn meal and starch,	67
Corn meal and sugar,	54

To further test this, several trials were made with egg albumen, which when digested by itself was wholly digested; but the addition of starch or sugar diminished its digestibility, while the two added and a little corn oil, making its composition more nearly like a natural feed, reduced very much the digestibility of the albumen.

Experimenters have assumed that in a compounded ration the results are the same as with each separate component of the ration. Considerable evidence may be brought forward to show the liability of error in making this assumption. Let us note the experiments of Malfatti[4] made upon himself with maize flour, and then with maize flour and butter, and again with maize flour and cheese. The per cent. of the different parts remaining in the faeces are given—

	Maize flour.	Maize flour and butter.	Maize flour and cheese.
Dry substance,	6.30	7.96	4.20
Nitrogen,	18.28	31.54	7.31
Fat,	42.14	56.03	9.34
Carbohydrates,	3.42	3.69	2.32

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[1] Annual Report Wisconsin Experiment Station, 1885.

[2] Bied. Centr. 1884, 751–755.

[3] Armsby's Manual of Cattle Feeding, 244.

[4] Bied. Centr. **15**, 40–41.

We may further draw from our experiments in artificial digestion[1] of the albuminoids of fodders, in corroboration of the same—

	Per cent. in ration digested (calculated).	Per cent. digested separately.
Ensilage, ...	73.56	61.35
Corn meal, ...	89.87	86.15
Wheat bran, . . .	83.06	83.26

When a method shall have been perfected whereby the digestibility of the other constituents of a fodder may be determined, a much more correct knowledge of the real nutritive value of our feeding-stuffs may be had; and I think chemists will soon find a means of measuring the other digestible portions. Then we shall be able to determine the nutritive value of a fodder in the laboratory, where we can have the whole process under control, eliminating the almost uncontrollable influences—the individuality of the animal, nervous influences, environments, temperature, and the necessary compounding of a ration—which in animal digestion enter in to vitiate the results.

GENEVA, N. Y., *August* 17, 1886.

ON THE SOLUBILITY OF MANGANESE SULPHIDE IN MELTING POTASSIUM SULPHIDE.

BY EDO CLAASSEN.

When experimenting with vanadiferous magnetite for the purpose of determining the best way to extract from it all vanadium, the pulverised ore was oxidised and brought into a very finely divided state by a process to be described later in a paper on the extraction of vanadium. This powder was mixed with six times its weight of equal parts of sulphur and potassium carbonate, then melted in a well-covered porcelain crucible until almost all free sulphur was gone, *i. e.* until hardly a flame of burning sulphur could be seen outside of the vessel. When cold, the crucible and contents were lixiviated with hot water, the filtrate acidulated with nitric acid in a beaker, mixed, after having been heated for some time, with an excess of potassium carbonate, heated again and brought to perfect dryness in a porcelain dish. This remnant, amounting to more than four times the weight of the magnetite, gave, when melted in a crucible, a dark bluish-green mass, which, after treatment with water, furnished a red solution and a brownish deposit.

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[1] Fourth Annual Report N. Y. Experiment Station, 316.

The dark bluish-green color of the mass was evidently due to the presence in it of potassium manganate, which, as is well known, is decomposed by being dissolved in water, thereby giving a solution of permanganate and a precipitate of hydrated manganese peroxide. By the intensity of the color it was furthermore plainly proved that the amount of manganese present was not inconsiderable.

ON THE EXTRACTION OF VANADIUM AND CHROMIUM FROM IRON ORES, PARTICULARLY FROM MAGNETITE.

By Edo Claassen.

In all treatises on the extraction of vanadium from iron ores, which have come into my hands, it is recommended to use the ore for the melting process with sulphur and soda, or with saltpetre and soda, in a very finely pulverised and bolted state; in a few places a repetition of the melting is spoken of as a sure means of getting out all the vanadium present in the ore. The result may be satisfactory if iron ores, such as limonite, which are easily converted into impalpable powders, are used. In cases, however, where ores of considerable hardness, like magnetite, are to be extracted and analysed, the pulverisation alone will not, as many experiments made by me have proved, bring the substance to be operated upon into such a form and condition that, after melting, even if the work is repeated several times, the whole of the vanadium present can with certainty be expected to be transformed into a combination soluble in water.

The chief object, therefore, of my experiments described below was to find out in cases where hard ores, for instance magnetite, are to be dealt with, a short and simple way to bring these into the condition of the finest powders. Mechanical power proved to be insufficient for this purpose, as samples of magnetite brought into a very fine powder were, after ignition with soda and saltpetre, as also with soda and sulphur, and extraction with hot water, still partly magnetic, and, as was shown by special tests, they still contained some vanadium. The following method was finally resorted to, and it gave the desired result in a perfectly satisfactory way: A quantity of very finely pulverised magnetite was mixed in a capacious dish with an equal weight of water, and then with double its weight of sulphuric acid of 1.840 specific gravity; the contents of the dish became quite hot, and hence it was thought advisable to cover the vessel, so that any loss of substance might be avoided. When the reaction had ceased, the mixture in the dish was found to be in a nearly dry state. It was now transferred into a platinum crucible and heated, at first slowly, then after a time with a considerable increase of heat, until the water, then the sulphuric anhydride, and at last the sulphur dioxide formed, were entirely gone. The residue in the crucible, now probably being the oxidised ore, formed an impalpable powder of a red color, and of the greatest fineness. As will be shown below, it was in exactly the state of division wanted. I separated it into two parts and treated them as follows:

I. *Treatment with Soda and Sulphur, etc.*—One portion of the powder was mixed with six times its weight of equal parts of soda and sulphur, then brought into a porcelain crucible, which was now well covered and exposed to gradually increasing heat, until most of the free sulphur was volatilised, *i. e.* until a flame of burning sulphur was no longer visible outside the crucible. When nearly cold the contents of the crucible were thoroughly extracted with hot water, then filtered and the filtrate acidulated with dilute nitric acid, carefully avoiding loss in consequence of the escape of gas, and then set aside for some time. The liquid was now separated by means of a filter, the precipitate on it washed several times with water, and then brought to perfect dryness. By treating the dry precipitate with carbon disulphide, the free sulphur was easily removed, leaving the vanadium sulphide as a chocolate-brown powder. This, together with the filter, was incinerated in a porcelain crucible, the residue from the evaporated filtrate obtained above, in which there is always a small amount of vanadium present, added to it, and also a small quantity of soda, and the whole ignited. The melted mass, poured on a fragment of porcelain, showed, after cooling, a dark bluish-green color *caused by some sodium manganate present.* It was extracted with hot water, the filtered liquid, contained in a flask, mixed with a good deal of ammonium nitrate and boiled, until the smell of ammonia had nearly disappeared. If, after another addition of a little ammonium nitrate, a smell of ammonia is again produced, some more should be added, and the boiling, as well as the addition of a new portion of this salt, should be continued until no smell is evolved after again operating in the same way. Not a trace of the vanadic acid is reduced in this way, which is often the case when neutralising is effected by dilute nitric acid, thus causing the escape of a certain amount of vanadium. However, instead of adding ammonium nitrate, it may be allowed, in cases where a small loss of vanadium is not objected to, to make use of the old method just mentioned of neutralising the alkaline liquid by dilute nitric acid, provided the mixing is done with great care, with constant stirring, always keeping in mind that the reaction of the liquid should never, not even partly or for a moment, turn acid, but always remain at the end a little alkaline.

The liquid, thus treated with ammonium nitrate, was filtered, precipitated with neutral lead acetate (or nitrate), the precipitate washed with water, put together with the filter into a flask, mixed with a sufficient quantity of chlorhydric acid and alcohol, and digested for some time. The precipitate formed by this operation was separated from the green liquid, the filter washed with alcohol, the alcoholic liquids united, evaporated or distilled in a beaker or flask, the remnant mixed with water, treated with hydrogen sulphide, filtered, concentrated by evaporation, poured into a wide porcelain crucible, evaporated on the water bath, perfectly dried, and ignited. The remaining vanadium pentoxide, which is mostly impure, and generally contains a little vanadium oxide, gave, repeatedly moistened with a solution of ammonium nitrate and ignited and then extracted for purification with an ammonium carbonate solution or with ammonia, a liquid which, when filtered, evaporated and ignited again in a weighed crucible, left the exact amount of all the vanadium pentoxide present.

The residue on the filter left after the lixiviation of the melted mass obtained by the treatment with soda and sulphur was subjected once more to the same melting process and to all the subsequent operations, for the purpose of showing that all of the vanadium was extracted by *but one* process. The result was a good one, as only a trace of vanadium pentoxide was obtained. The residue left the second time on the filter after melting and lixiviation was then treated as follows: It was dried, extracted with carbon disulphide and digested with concentrated chlorhydric acid, which dissolved but a little of it, giving a solution not containing any vanadium or chromium. Most of the residue left here was then by digestion with concentrated nitric acid brought into solution, in which hardly more than a trace of vanadium and no trace of chromium were ascertained. It may be stated here that by the operations just described all the chromium of the ore was left undissolved; all of it was therefore evidently to be looked for in the small balance of the ore now left after treatment in the above manner. This balance was melted after drying for the extraction of the chromium and also of the vanadium, which had perhaps escaped the solvents, with six times its weight of equal parts of soda and saltpetre, the melted mass lixiviated with hot water and treated as described below under II. While all the chromium of the ore could be stated to be present in this solution, only traces of vanadium could be found in it. I think the above experiments prove clearly that by Treatment I all the vanadium of the ore finds its way into the solution, while all the chromium is left undissolved. This method of extracting and separating the vanadium is therefore highly to be recommended, particularly if the estimation of this element only is the point aimed at. If, however, it is the object of the analysis to determine the quantity of the chromium as well as that of the vanadium, it may be equally or even more advantageous to make use of the mode of extraction described below under II, which affords nearly as good results, as regards the separation of vanadium, as I.

II. *Treatment with Soda and Saltpetre, etc.*—The other portion of the ore, treated with concentrated sulphuric acid, etc. (see above), was mixed with six times its weight of equal parts of soda and saltpetre, ignited, and perfectly extracted with hot water. The residue was subjected once more to the same operation, and it was only the solution of this last melted mass that was used for the detection and estimation of any vanadium and chromium still left in it. For this purpose it was heated with such an amount of ammonium nitrate that, when the smell of ammonia had disappeared, the addition of a new portion of that salt did not produce it again. The liquid was now precipitated by neutral lead acetate, the precipitate collected on a filter, washed thoroughly, and while still moist digested with chlorhydric acid and alcohol; the filtrate evaporated to remove, besides the alcohol, most of the acid; then, after dilution with water, treated with hydrogen sulphide, filtered, evaporated and ignited. The residue, containing all the vanadium and chromium brought into solution by the last melting process, was mixed, for the purpose of separating these two elements, with soda and sulphur in the proportion of 1 : 3 : 3, and ignited until almost all free sulphur was gone. When cold, the crucible with its contents was put into boiling water; after filtering, all the chromium present was found on the filter, and all the vanadium in the solution. The filter was incinerated, and the residue mixed with six times its weight of equal parts of soda and saltpetre. After melting, the mass was dissolved in hot water, the solution filtered and precipitated as usual in form of lead chromate.

The vanadiferous filtrate, however, was acidulated in a beaker with diluted nitric acid and filtered after some time; the residue on the filter, after drying, was extracted with carbon disulphide, mixed with the evaporated filtrate before obtained, and melted. The melted mass, poured on a piece of porcelain, was dissolved in hot water, filtered, boiled for some time, after addition of ammonium chloride, then filtered again and evaporated so far that, after cooling and stirring for a while, no separation of crystals had taken place. Into this solution a lump of ammonium chloride was deposited large enough not to be dissolved entirely; the precipitate of ammonium metavanadate, which separated after a time, was collected on a filter, washed with a sufficient quantity of a saturated solution of ammonium chloride, dried and ignited. For the purpose of purification the remaining vanadium pentoxide, after it was moistened with a solution of ammonium nitrate and ignited, was dissolved in ammonia, and the solution evaporated until ammonia could scarcely be detected by the odor, then filtered, evaporated to dryness and ignited. Very exact analyses demand the collection of the small amount of ammonium metavanadate always remaining in the filtrate, and this is therefore evaporated to dryness and ignited. The residue is digested with some concentrated ammonia, the solution filtered, and precipitated with alcohol. The precipitate, dissolved in a little water, will give a solution, furnishing, when treated as above, with a lump of ammonium chloride, the small residue of ammonium metavanadate. The ignited mass (see above) may also—and this is a good method, after treatment with ammonia, heating to drive off the excess of ammonia, and filtration—be precipitated by lead acetate. The precipitate is then suspended in water, acidulated with nitric acid, and decomposed by means of hydrogen sulphide.[1] In this way a filtrate is formed which leaves on evaporation and ignition the whole balance of the vanadium pentoxide.

It was already mentioned before that the purpose of melting the ore for the second time with soda and saltpetre was to determine if any vanadium and chromium, and how much, were not extracted the first time. The result of these operations was that scarcely a trace of chromium and but little more than a trace of vanadium were found, so that, if the work is done in a careful way, a repetition of all the operations will surely be unnecessary.

A comparison of the two methods of treatment described shows that Treatment I is always to be preferred, if it is desired to estimate only the vanadium, because it furnishes at once a solution free from chromium, and the quantity of vanadium left in the ore is smaller, and, further, because a large porcelain crucible can generally be had more easily than a large platinum one.

It is, however, a fact known to every analytical chemist that platinum crucibles are always preferred to such of porcelain, provided there is no objection to use them. With this point in view, it seemed to me to be both interesting and important to ascertain if an addition of a smaller quantity of soda and saltpetre to the treated ore might suffice to decompose it perfectly. The ore or the residue left each time after the ignition and extraction with water on the filter was therefore subjected to these operations three times: the first time it was made strongly alkaline by means of soda and then mixed with the third part of its weight of saltpetre; the second time the residue on the filter was mixed with the third part of each of soda and saltpetre, and the third time double the quantity of an equal weight of each one was mixed with the residue. The result of the melting processes was that the solution obtained the first time was yellow; that of the second time yellowish, and that of the third time hardly yellowish; and while the amount of vanadium and chromium was the largest in the first solution, there was still an appreciable quantity of both in the second; but a little, however, of both in the third. On comparing this result with that above obtained, when the melting was done once only with a considerable quantity of soda and saltpetre, it seems to me clear that, in order to obtain a good result, it is not only advisable, but necessary, to add to the prepared ore about three times its weight of each of these substances.

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[1] A precipitate of lead chromate and lead vanadate was suspended in water, acidulated with nitric acid, and treated with sulphuretted hydrogen gas, which decomposed it easily and perfectly. A precipitate, however, of the above lead compounds and of lead sulphate (the last one in considerable excess) did not give an equally good result, although the gas was passed until a strong smell of it remained after standing. It was observed that the smell disappeared again entirely after several hours, although the vessel was well closed, thus showing that a complete decomposition had not taken place. As the same result was obtained after repeated treatment, the precipitate was separated by a filter from the liquid, and both subjected to several tests, which proved that the precipitate contained lead sulphate, lead vanadate and lead chromate, besides lead sulphide, while in the filtrate sulphuric, vanadic and chromic acids were found. The above method of decomposing a precipitate of lead vanadate and lead chromate is therefore without doubt a good one only if no lead sulphate, or but a little of it, is present; if, however, a large quantity of it is present, it would be a troublesome and tedious operation to effect the necessary thorough decomposition of the precipitate in this manner. In such a case treatment with chlorhydric acid and alcohol will answer the purpose quickly and satisfactorily.

WILLIAM RIPLEY NICHOLS.

The death of Prof. William Ripley Nichols removes from us not only one of the most eminent of American chemists, but also one of the most influential of American educators. Prof. Nichols combined in a rare degree the love of teaching and the love of science, and he introduced into his teaching the same scientific spirit which he showed in solving difficult problems pertaining to sanitary chemistry. He was one of the first to emphasise the importance of laboratory work even in the teaching of elementary chemistry. Yet he never made a fetich of this method of instruction, and always recognised the fact that the necessity for hard study was not removed by the use of this now fashionable mode of teaching. So he required his students to obtain not only skill in manipulation and accurate information concerning the properties of compounds, but also a thorough knowledge of the theoretical views that lie at the foundation of modern chemistry. Prof. Nichols believed that a thorough laboratory training in general chemistry was the best method for cultivating the habit of accurate observation and for teaching the fundamental rules for scientific investigation to all students, whether they were in later years to pursue the study of chemistry or any other branch of science.

William Ripley Nichols graduated from the Roxbury Latin School at the age of sixteen. He then spent two years in travel and study in Europe, and returned and entered Harvard University. Although a proficient and interested student of the classics, yet in a few months he became convinced that a purely scientific training would best fit him for the duties of manhood, and he withdrew from the University and connected himself as a student with the Massachusetts Institute of Technology, then in its infancy, and graduated from this school with the class of 1869. His proficiency in his favorite science caused him to be chosen immediately instructor in chemistry in the Institute; in 1870 he was chosen assistant professor, and in 1872 he was called to fill the chair of General Chemistry in the Institute of Technology, and he retained this position until his death.

His early researches were in the field of inorganic chemistry, but in 1870 he turned his attention to sanitary chemistry, and to what afterwards became his specialty—water supply and questions related to it. He was employed by the Massachusetts State Board of Health to examine into the sanitary condition of the prominent rivers of the State, and often consulted by this Board upon matters relating to the public health. His aid was invoked by the Water Boards of many cities, and his opinion on subjects relating to water supply had great weight not only in America, but also throughout Europe. He received a medal and diploma from the London Health Exhibition in recognition of his eminence as an authority and of aid rendered. His publications of considerable length, relating to sanitary chemistry, number forty-four. The most important among them is his well-known work, "Water Supply, Chemical and Sanitary," published in 1883.

But Prof. Nichols did not confine his literary activity to the field of sanitary chemistry. In conjunction with Prof. John Trowbridge and Dr. Samuel Kneeland he prepared the "Annals of Scientific Discovery" for 1869 and for 1870. He abridged and revised Eliot and Storer's "Manual of Inorganic Chemistry," and thus he produced the well-known Eliot and Storer's "Elementary Manual of Chemistry." He also revised the "Qualitative Analysis" by the same authors, and prepared, in connection with the writer, a book entitled "Laboratory Experiments."

Prof. Nichols brought to his work a strong frame, remarkable energy and patient application. His personal devotion to the interests of the Massachusetts Institute of Technology impressed all who knew him. No labor was too hard, no effort too great, if his loved Institute was to receive benefit from it. In 1881, in consequence, doubtless, of overwork, the disease which finally ended his life attacked him, and his last five years were years of continual pain and weakness. Twice he sought relief by aid of the surgeon's knife, but the second operation resulted fatally, and he died at Hamburg, Germany, on July 14, 1886, aged 39 years. His domestic life had been singularly happy, and to the devotion and care of his wife was due, in no small degree, the courage with which he fought deadly disease during these long years and the determination which enabled him while an invalid to continue his work with unabated zeal. His career had been a busy and useful one, and his upright character and his love of science will continue to live in the minds and aims of the many students who came under his influence.

L. M. NORTON.

NOTES.

Action of an Electric Current upon Anhydrous Hydrofluoric Acid.

In a paper[1] presented to the French Academy of Sciences during the month of July, H. Masson describes the results he obtained by subjecting anhydrous hydrofluoric acid to electrolysis. The hydrofluoric acid made by heating carefully dried potassium hydrogen fluoride (KF.HF) is placed in a platinum U tube, cooled down to —50° C. and then subjected to the action of an electric current from twenty Bunsen elements. The platinum U tube is provided with small platinum tubes at the upper ends, for the escape of the gases formed, and is closed with stoppers made of fluor spar, through which the platinum electrodes pass.

From the negative pole hydrogen is evolved, while from the positive pole a colorless gas escapes, in which crystallised silicon and boron burn, forming fluorides. Powdered arsenic and antimony, as well as sulphur and iodine, take fire when brought into contact with this gas, the last losing its color. In contact with water the gas is decomposed, yielding ozone and hydrofluoric acid. The metals are also attacked by it; powdered iron and manganese when heated burn in it brilliantly. Organic substances are violently attacked. Cork is at once carbonised and takes fire, while alcohol, ether, benzene, turpentine oil and petroleum also burn in contact with the gas. When the hydrogen from the negative pole comes in contact with the gas evolved from the positive, they combine with a violent explosion.

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[1] Compt. Rend. **103**, 202–205. Preliminary Note, *ibid.* **102**, 1543.

As a mixture of ozone and hydrofluoric acid does not show any of these reactions, and as the hydrofluoric acid used was shown to be absolutely free from chlorine, the author concludes that the gas evolved from the positive pole in the electrolysis of hydrofluoric acid is either fluorine or hydrogen perfluoride. In a later paper[1] on the same subject, he shows that this active gas is also obtained by the electrolysis of the fused potassium hydrogen fluoride (KF.HF), and that it undoubtedly is fluorine, and not hydrogen perfluoride. This is shown by the fact that it yields no hydrogen when passed over powdered iron heated to redness, and by the fact that the increase in weight which the iron shows in this experiment (due to the formation of iron fluoride) corresponds very nearly exactly to the quantity of hydrogen evolved from the negative pole, which was collected and measured.

W. R. O.

U. S. DEPARTMENT OF AGRICULTURE,
DIVISION OF CHEMISTRY,
WASHINGTON, D. C., *December* 9, 1886.

PROF. IRA REMSEN,
Editor American Chemical Journal.

Dear Sir :—In my recent address before Sec. C, A. A. A. S., at Buffalo, I gave a brief review of the present knowledge of nitrification and denitrification in their relations to plant-growth. In this summary I omitted to mention the paper[2] of Dr. Alfred Springer on denitrifying ferments. I feel quite sure that to him equally with Gayon and Dupetit belongs the honor of having discovered this ferment.

Hoping thus to do him tardy justice,

I am faithfully,

H. W. WILEY.

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[1] Compt. Rend. **103**, 256-258.

[2] This Journal **4**, No. 6. Proceedings Ohio Mechanics' Institute **2**, No. I.

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